PROCESSING, CHEMISTRY AND APPLICATIONS OF LAC

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Processing, Chemistry and Applications of Lac

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Foreword

COLLECTED as the minor forest produce and cultivated since time immemorial in India, lac still enjoys the monopoly of non-toxic, biodegradable, natural and safe resin for variety of uses in industries. India being the largest producer, processor and exporter, has the distinction of having full-fledged institute for research on all aspects of lac. However, the available information on its processing, chemistry and applications under one spine was wanted for long. The chapters in "*Processing, Chemistry and Applications of Lac*" have been contributed by experts and scientists of long experience in the respective areas and the effort to document available information in the form of a book is commendable.

The book provides an up-to-date information on processing, chemistry of lac resin and its constituents, physical characterization, spectral characteristics, electrical properties, application in various industries, comparison with synthetic alternatives, quality and its evaluation, Indian standards on lac and lac-based products and also outlines future scope and lines of work. There was a need to document available indigenous traditional knowledge as an IPR protection measure as well.

Utility of this book is enhanced by the future perspective of the increased global demand for the natural materials used for human contact and consumption. The book will be useful to all concerned with lac, especially processors, entrepreneurs, users, exporters, traders and researchers. I compliment the authors for their initiative in bringing out the comprehensive information in this book on lac processing, chemistry and applications.

(S. Ayyappan)
Secretary
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Preface

LAC is collected as a minor forest produce and used for applications in pharmaceuticals, cosmetics and surface coatings since time immemorial. Organized research on lac was started in 1924 in India after realization of its commercial potential world-over. Research as well as documentation on all aspects of production, processing, product development and use diversification has led to generation of voluminous information. However, the information was not available under one spine.

This book covers processing, chemistry of lac and its constituents, physical characterization, various physico-chemical, electrical properties, industrial and other applications, quality and its evaluation, standards on lac and lac-based products and also on outlining the future scope of the work. The documentation of the indigenous traditional knowledge is likely to serve as an IP protection measure as well.

India enjoyed a global monopoly over lac trade till 1970s when some other south-east Asian countries, *viz.*, Thailand, Indonesia, Vietnam and some other areas in China started producing lac. India touched a peak production of about 50,000 tonnes in 1940s. During 1960-2000, the demand of lac-based products declined due to competition and emerging trend of the use of synthetics as substitutes. By the end of 20th century, the realization emerged for natural and safe materials for human contact and consumption. This trend has enhanced demand again and revived lac production considerably.

We thank all the contributors whole-heartedly who responded to our request and provided specialized information in interesting reading and easy to understand language. Valuable inputs and suggestions from Dr Mangala Rai, former DG; Dr Nawab Ali, former DDG (Agricultural Engineering); Dr P Chandra, Director, CIAE, are gratefully acknowledged. Keen interest and encouragement by Dr T P Trivedi, Project Director (DIPA) deserves appreciation in bringing out this book. The authors are thankful for assistance provided by Dr S Srivastava, Mr M F Ansari, Dr R Ramani, Dr (Er) N.Prasad, Dr S K Giri, Shri D Ganguli and Shri R P Srivastava of this institute.

New Delhi
Namkum, Ranchi

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Lac: an introduction

B Baboo[1] and *D N Goswami*[2]

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LAC is derived from the Sanskrit word "*lakh*" which means 100,000 and refers to the vast swarms of insect larvae that cover twigs of host trees during brood season. Lac is a general term used in the trade for all forms of natural resin, which is secreted by the tiny lac insects on certain host trees, principally found in India, Thailand, China and Indonesia. Lac history can be traced back to Vedic period (C.1500 to 500 B C). *Atharva Veda* devotes a chapter containing vivid description of '*Laksha*'(lac insect) and its use in invigorating potion and wound healing. In the great epic, *Mahabharata*, *Purochak* constructed '*Lakshagriha*' (house of lac) at the instance of Kauravas for killing Pandavas. The works of a number of foreign travellers reveal the trade of lac from India to a number of countries during post-Vedic and medieval periods.

Use of *lac* is known in India for centuries especially as the source of dye and decorative coatings. Records from the late 1500's reveal its use for decorating public buildings during Moghul ruler Akbar (Martin, 1982). Its use in China is reported, for application molten waxes to oranges and lemons, as early as 12th or 13th century. It was also known to ancient Greek and Roman writers and widely used in Europe for furniture finishing during late fifteenth century (Class, 1991). The superb adhesive quality of the resin made it useful for setting jewels and sword hilts as well as repairing broken pottery. The residue left after extraction of the dye was made into a grinding wheel for jade – the technique is used even today.

Shellac (refined commercial form of lac resin) and different shellac-based products began to make their way into European commerce and industry after historical journey of Marco Polo to Orient in late 13th century. Detailed description about the cultivation, harvesting, processing and use of lac is available in the literature as early as 1534. Painters started use of shellac resin, shellac dye and shellac wax not only to create their masterpieces, but also to provide them with a protective finish by the mid-17th century. Shellac became the coating of choice for costly furniture, woodcarvings, and turnings for craftsmen and artisans. Even today some of the finest museum pieces still have their original shellac finish.

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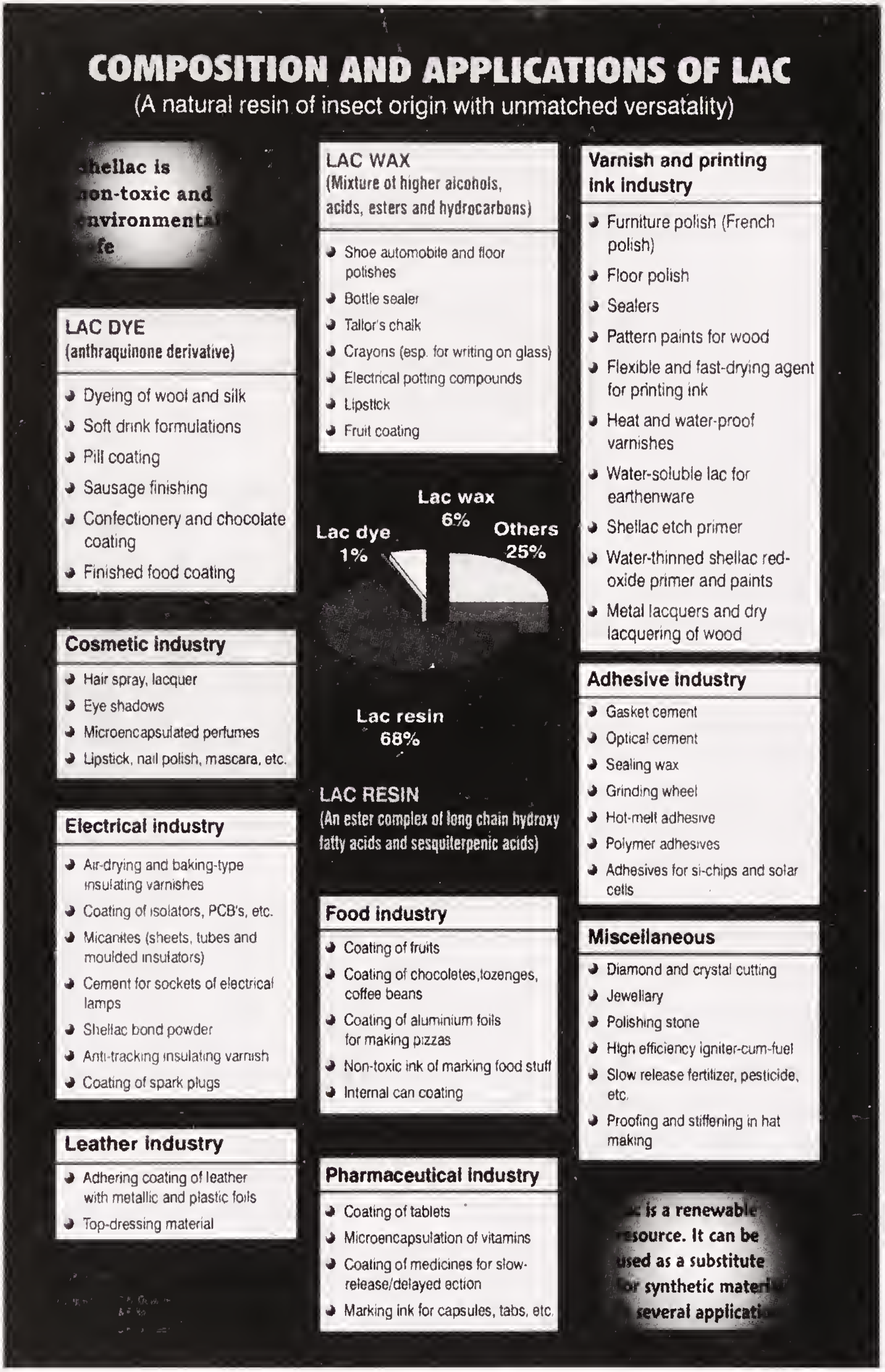

COMPOSITION AND APPLICATIONS OF LAC

(A natural resin of insect origin with unmatched versatality)

hellac is on-toxic and nvironment fe

LAC DYE
(anthraquinone derivative)

- Dyeing of wool and silk
- Soft drink formulations
- Pill coating
- Sausage finishing
- Confectionery and chocolate coating
- Finished food coating

Cosmetic industry

- Hair spray, lacquer
- Eye shadows
- Microencapsulated perfumes
- Lipstick, nail polish, mascara, etc.

Electrical industry

- Air-drying and baking-type insulating varnishes
- Coating of isolators, PCB's, etc.
- Micanites (sheets, tubes and moulded insulators)
- Cement for sockets of electrical lamps
- Shellac bond powder
- Anti-tracking insulating varnish
- Coating of spark plugs

Leather industry

- Adhering coating of leather with metallic and plastic foils
- Top-dressing material

LAC WAX
(Mixture of higher alcohols, acids, esters and hydrocarbons)

- Shoe automobile and floor polishes
- Bottle sealer
- Tailor's chalk
- Crayons (esp. for writing on glass)
- Electrical potting compounds
- Lipstick
- Fruit coating

LAC RESIN
(An ester complex of long chain hydroxy fatty acids and sesquiterpenic acids)

Food industry

- Coating of fruits
- Coating of chocoletes,lozenges, coffee beans
- Coating of aluminium foils for making pizzas
- Non-toxic ink of marking food stuff
- Internal can coating

Pharmaceutical industry

- Coating of tablets
- Microencapsulation of vitamins
- Coating of medicines for slow-release/delayed action
- Marking ink for capsules, tabs, etc.

Varnish and printing ink industry

- Furniture polish (French polish)
- Floor polish
- Sealers
- Pattern paints for wood
- Flexible and fast-drying agent for printing ink
- Heat and water-proof varnishes
- Water-soluble lac for earthenware
- Shellac etch primer
- Water-thinned shellac red-oxide primer and paints
- Metal lacquers and dry lacquering of wood

Adhesive industry

- Gasket cement
- Optical cement
- Sealing wax
- Grinding wheel
- Hot-melt adhesive
- Polymer adhesives
- Adhesives for si-chips and solar cells

Miscellaneous

- Diamond and crystal cutting
- Jewellary
- Polishing stone
- High efficiency igniter-cum-fuel
- Slow release fertilizer, pesticide, etc.
- Proofing and stiffening in hat making

is a renewable esource. It can be used as a substitute synthetic mate several applicati

Fig. 1.1. Composition and aplications of lac

Two English brothers had set up a big commercial lac industry in India in 1855 mainly for supply of lac dye. First record of the lac dye export to Europe was, however, in 1607, which flourished up to close of 19th century till the advent of aniline dyes. Subsequently, the lac resin exports picked up particularly for use in gramophone industry, varnishes, etc. The use of lac has now diversified into a wide range of areas (Fig.1.1).

LAC: A PRODUCT OF PLANT AND INSECT INTERACTION

Shellac is derived from the hardened secretion of lac insect *Kerria* spp. feeding on resiniferous trees and bushes cultivated in India, Burma, Thailand, Laos, Cambodia, China and Vietnam. The resin is secreted as a covering for the insect larvae. Even though 87 species of lac insects have been reported world-wide, only a few species are useful for commercial lac production.

Lac production

Lac was primarily collected from the forests till the end of 19th century and during the beginning of 20th century, its cultivation started due to its varieties of applications and increasing demand. The Indian Lac Research Institute provided a scientific cult to lac cultivation after its establishment in 1924 at Namkum. Lac production in India is contributed by Jharkhand, Chhattisgarh, Madhya Pradesh, West Bengal, Orissa and Maharashtra. Lac-growing regions are generally dominated by economically resource-constrained tribal population. The areas comprise high proportions of forest and uncultivable land with poor irrigation facilities and the areas possess low literacy levels, high proportion of scheduled tribes and population below poverty line. Considering available resources, economic and cultural aspects of the inhabitants, lac cultivation is ideally suitable for livelihood enhancement/economic progress in such regions. Lac cultivation has proved to be an important source of cash income in such areas, especially, at the failure of the national agricultural crops.

There had been a major drop in lac production in 1998, due to crop failure in Jharkhand because of adverse climate (Fig.1.2). The production has recovered to normal levels in the recent years. Speedy recovery of lac production after failures is constrained by storability and transportation of brood lac over long distances. Therefore, there is a greater need to expand production base to a larger area over different agro-climatic regions of the country and to establish brood lac production farms in different locations to ensure production stability in the country. Interaction with representatives of lac industry indicated a very large unrealized demand for lac in the country and overseas. It is felt that there is an ample scope for aiming a quantum increase in the lac production to realise this untapped potential.

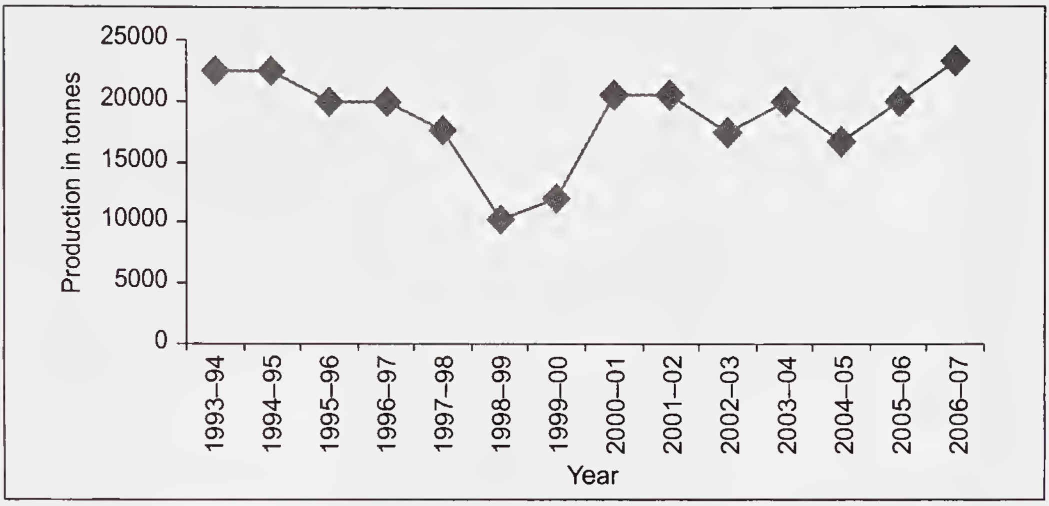

Fig. 1.2. Production of stick-lac in India

Lac insects and lac hosts

In India, lac cultivation is done mainly through culture of Indian lac insect *Kerria lacca* on hosts, viz. *kusum* (*Schleichera oleosa*), *palas* (*Butea monosperma*) and *ber* (*Ziziphus mauritiana*). Two lac crops are produced in a year corresponding to two cycles completed by insect in an year. The Indian lac insect has two strains, *kusmi* and *rangeeni*, differing in life-cycle pattern, host-plant preference and quality of lac (resin) produced. *Kusmi* insect is characterized by high productivity and best quality of resin produced in the world. To produce 1 kg of lac resin around 50,000 insects are required (Table 1.1).

Table 1.1. Important host trees for lac insects in different lac-producing countries

Country	Common host trees	Scientific name	Family
India, Principal hosts	*Kusum*	*Schleichera oleosa* (Lour.) oken	Sapindaceae
	Palas/dhak	*Butea monosperma* (Lam.) Taub.	Leguminosae
	Ber	*Ziziphus mauritiana* Lam.	Rhamnaceae
India, other hosts	*Khair/cutch*	*Acacia catechu* (L.f.)Willd.	Leguminosae
	Babul	*A. nilotica* (L.) Delile	Leguminosae
	Arhar	*Cajanus cajan* (L.) Millsp.	Leguminosae
	Sappan	*Caesalpinea sappan* L.	Leguminosae
	Pipal	*Ficus religiosa* L.	Moraceae
	Banyan	*Ficus benghalensis*	Moraceae
Thailand, most common	Rain tree	*Samanea saman* (Jacq.) Merr.	Leguminosae
China	*Arhar*	*Cajanus cajan* (L.) Millsp.	Leguminosae
		Dalbergia balencea.	Leguminosae
		Hibiscus spp.	Malvaceae

Climate

Lac insects can be cultured over a fairly wide range of tropics and sub-tropics and on a large number of host trees, 40° north and south of equator. Moderately hot to mild temperature and humid conditions are favourable for lac culture. Thus, lac production is limited to a few south, south-east and east Asian countries in the tropical forests region. A large part of India offers climate suitable for lac production.

MERITS OF LAC CULTIVATION IN INDIA

- It is good source of livelihood of limited-resource farmers, tribals inhabiting sub-hilly tracts.
- It requires no irrigation, meagre fertilizers, labour and pesticides.
- A good crop for marginal and degraded lands; no competition for land or farm operation with agricultural/ horticultural crops.
- Highly remunerative cultivation, a hectare of *ber* plantation with *kusmi* lac cultivation can provide net returns of Rs 3 to 5 lakh/year.
- It is like an insurance crop especially, during drought years as the crop is very good during such adverse climate.
- Lac cultivation involves significant women participation and helps ecosystem development.
- Vast natural resources of untapped lac hosts are available for commercial exploitation.
- Rich traditional knowledge and skill in production and processing are available.
- Good infrastructural support for research, development and export is available.
- Nature's unique gift of *kusmi* lac is not available in any other country.

LAC PRODUCING COUNTRIES

India, Thailand and the People's Republic of China are the major producers of stick-lac and its derivatives; the first two are also the major exporters of lac products and share almost equally export market; while China's production is mainly consumed in the domestic market. Indonesia, Bangladesh, Myanmar, Vietnam and Sri Lanka are the minor producers of lac. The present production of lac in India is about 20,000 tonnes per annum.

The main lac-collecting centres in Thailand are Chiengmai, Obol, Denchai and Rahang. Bangkok is, however, the main trading centre. Thailand's production and exports of lac commenced in 1950s and progressively eroded India's share of the international market through keen pricing. Recent exports have been of the order of 7,000 tonnes annually, mainly of the partially refined seedlac.

China's main cultivation area for stick-lac is the province of Yunnan, where recent annual production volumes have been 4,000 to 5,000 tonnes of crude stick-lac and 2,000 to 3,000 tonnes of processed shellac, together with some quantity of lac dye. Production has also been initiated on a smaller scale in the province of Fujian since mid-1950s. Exports of shellac are comparatively small at approximately 500 tonnes per annum; Japan being its principal buyer. A Japanese company is operating a lac factory in Thailand.

Lac industrial scenario: national and international

In our country, the main lac-processing centre is at Balarampur, West Bengal, where lac is manufactured at cottage industry level. Besides, there are a few around at Kolkata (West Bengal), Chhattisgarh, Madhya Pradesh, Maharashtra and Jharkhand. In all, about 200 units of lac-processing centres are involved in the trade, in the country, ranging from very small to larger ones with the processing capacity of less than 100 kg to 5,000 kg per day. There are about 20 units in Germany, USA, China, Thailand and Japan. The individual capacities of these units are higher than an average Indian unit. A processing center is also reported at Pegu in Myanmar.

LAC COMPOSITION

Raw lac (stick-lac) contains resin, wax, dye, insect body, bark of host trees as well as other impurities. This is, therefore, refined to obtain purified material of commerce (called shellac). The chemical composition and constituents of shellac have been discussed in chapters 3 and 4. The lac resin is a polyester complex of long-chain hydroxyfatty acids and sesquiterpenic acids. Indian lac dye is a mixture of at least 5 anthraquinone derivatives called laccaic acids. Lac wax is complex mixture of long-chain acids, alcohols, esters and hydrocarbons.

LAC APPLICATIONS

Some general information about applications of lac are given as follows:

Resin

The first use of shellac as a protective coating appeared as early as 1590 in a work by an English writer who was sent to India to observe the country and its people. Commenting on the procedure for applying lac to wood still on the *lathe* he wrote “they take a piece of lac of what colour they will, and as they turne it when it commeth to his fashion they spread the lac upon the whole piece of wood which presently, with the heat of the turning (*melteth the waxe*) so that it entreth into the crestes and cleaveth unto it, about the thicknesse of a man’s naile: then they burnish it (over) with a broad straw or dry rushes so (cunningly) that all the woode is covered with all, and it shineth like glasse, most pleasant to behold, and continueth as long as the woode being well looked unto: in this sort they cover all kinde of household stuffe in India". It's interesting that many wood turners still finish this same method even today (Jewitt, 1935).

Wax

In the United States, waxes used on citrus initially were paraffin based in 1930's, evolved to solvent-based resins in late 1940's. Use of carnauba waxes was in vogue in late 1950's but became less popular due to lack of shine. Waxes containing shellac and various alkali soluble resins plus adjuvants were introduced in early 1960's and are being widely used in citrus-producing areas since then (Kaplan, 1986).

Dye

Vinaya texts of Buddhists described use of lac dye in dyeing of fabrics. Kalidasa's works contain descriptions of use of lac dye for cosmetic purposes. The original cultivation of lac was not for resin, but rather, for dye that gives the resin its characteristic colour. Use of lac dye can be traced back to 250 A.D., mentioned by Claudius Aelianus, a Roman writer, in a volume on natural history. The dye remained a valuable commodity until the mid-nineteenth century, when Perkins, an English chemist, synthesized first chemical 'aniline' dye, which killed natural dye industry. Ancient Chinese and Indian civilizations used the dye extracted from lac for dyeing silk, leather, as cosmetic rouge and a colouring for head ornaments.

Product standardization

Lac being an export commodity, quality evaluation, particularly acceptable at international level, is of utmost importance as it assures reliability/consumer confidence, quality related product price, desired product/by-product recovery and promotes healthy manufacturing and trade practices. The Institute is actively associated with the Bureau of Indian Standards, New Delhi for formulating and finalizing different standards for different forms of lac and lac-based products for stringent quality control in the country. The institute represents CHD 23 sub-committee of the BIS meant for lac and lac-based products.

Lac and lac products exports

Out of the different lac-based products exported during the VIII and IX Plan (Fig.1.3), there exists a tremendous potential for export of value-added lac-based products (dewaxed decolourized lac, bleached lac, lac dye, aleuritic acid, isoambrettolide) provided a stable price structure is maintained.

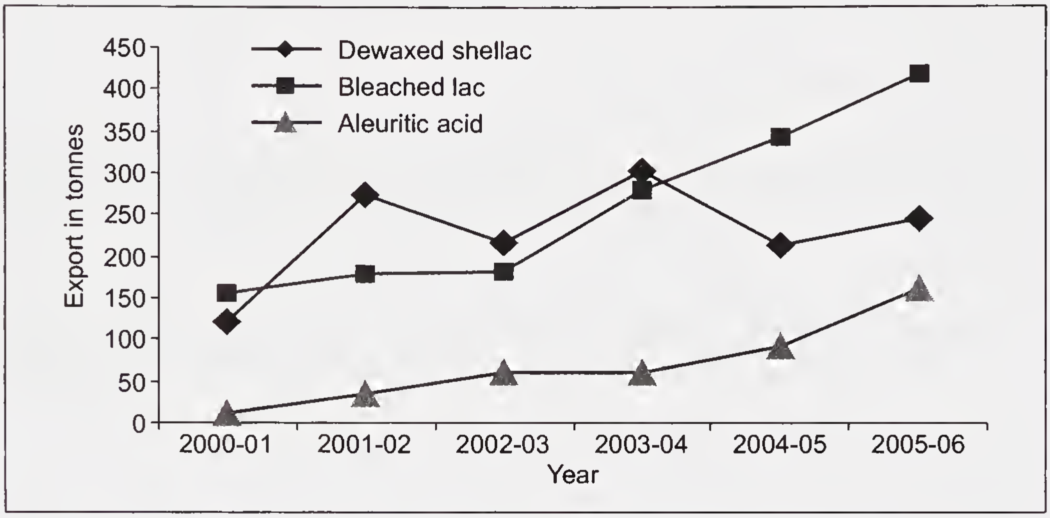

Fig. 1.3. Export of three value-added lac-based products–dewaxed shellac, bleached lac and aleuritic acid

LAC RELATED ORGANIZATIONS

Some of the organizations, which are engaged in the support of the lac industry and the trade in India, are as follows:

Indian Institute of Natural Resins and Gums, Ranchi

The Indian Institute of Natural Resins and Gums (IINRG), is the nodal Institute at the national level for research and development on all aspects of lac, production, on-farm and off-farm training on lac production; processing, training on lac processing, product development; manufacture of lac-based products; entrepreneurship development training; repository of information; consultancy and quality evaluation service of lac and lac-based products for entrepreneurs, lac exporters and also co-operation at the national and international levels for formulation of standards of different lac and lac-based products. Its quality evaluation laboratory has received licence for the Quality Management Systems Certification from the Bureau of Indian Standards, New Delhi, in accordance with IS/ISO 9001:2000 to render laboratory services for collection, analysis, testing and reporting of lac and lac-based product samples. Its website is www.icar.org.in/ilri.

Shellac and Forest Products Export Promotion Council, Kolkata

It is the nodal Export Promotion Council (formerly, Shellac Export Promotion Council, www.shellacepc.com) to promote exports of "Minor Forest Produce" and registering authority for related exporters under the Foreign Trade Policy. Its mission is "to enable and assist members of the Shellac Export Promotion Council to discharge their responsibilities and obligations under foreign trade policies and to strengthen the plans and initiatives for enhancing exports of shellac and lac-based products and to realize the full potential of exports from India through collective action."

It plays a catalytic role in promoting India's MFP exports, acting as a bridge between exporters and various government agencies to ensure smooth growth.

Institute of Forest Productivity, Ranchi

Institute of Forest Productivity (*www.envfor.nic.in/icfre/ifp/ifp.html*) is an research and development organization under the aegis of the Indian Council of Forestry Research and Education (ICFRE), Ministry of Environment and Forests, Government of India. It is mandated to steer, undertake and co-ordinate research, development and extension in forestry sector in Bihar, Jharkhand, West Bengal and Sikkim. The Institute aims at enhancing productivity of faunal and floral resources, conservation of biodiversity, eco-restoration of degraded lands and protection of diverse and fragile ecosystems unique to the region.

Jharkhand State Co-operative Lac Marketing and Procurement Federation Ltd, Ranchi

The main objective of the Federation (*www.jascolampf.com*) is to help lac growers in obtaining remunerative price of their produce. It also undertakes procurement of raw lac, processing into different products and their disposal.

Tribal Co-operative Marketing Development Federation of India Ltd, New Delhi

This is a body of Government of India (*www.trifed.co.in*) for sustainable development of nature's bounty for tribal people through marketing of non-wood produce. Besides other activities, it provides assured market and remunerative prices for tribal produce and undertakes price support operations wherever and whenever required.

FUTURE PERSPECTIVES

Stability of lac prices during the recent years despite steady increase in production is indicative of strong demand of lac. Feedback from lac industries also supports this contention. There is increased stress on use of eco-friendly and safe natural material particularly associated with human contact and consumption. Thus, very good increase in demand of lac is envisaged. There is already demand picking up for bleached lac, and lac-dye in food processing industry and aleuritic acid in perfumery.

Two-fold increase in demand for lac is anticipated over the next decade. Indian lac industry would have to assure steady supply and price of lac to meet demands. To match this, we have to develop and maintain a suitable pace of increase in lac production in the country to minimize any adverse impact on the processing and supply of lac.

Based on the current trend, it is envisaged that by 2012, there will be shortage of lac host-plants, particularly *palas* and *kusum*, due to their exploitation for timber and other purposes; increase in soil salinity, accompanied by decrease in water-table; decrease in working hands in rural areas due to migration to cities and increased education; increase in prices of inputs such as fertilizers and pesticides; higher level of air pollution especially, due to industries and vehicles; and abnormal changes in temperature due to climate change.

While increase in price of inputs such as pesticides, fertilizers, accompanied by water scarcity might not have direct impact on the lac cultivation and utilization, but migration of rural populace to urban areas, coupled with decreasing forest cover, insect mortality due to air pollution and abnormal temperature rise and loss of interest in farm-related activities could have an adverse impact on the lac production.

Despite the advantages of lac, the challenge posed by the cheaper available synthetic substitutes, constant product refinement and development of newer areas are imperative for sustaining existing application areas and to offset eroding areas. The consumption of lac is mainly due to several of its unique properties, making it virtually indispensable in certain areas of its application. Besides, demand for lac dye is also showing revival in food industry. Yet, complex interactions of various marketing forces, both intra- and extra-sectoral, might adversely affect the demand pattern of the commodities. A concerted effort is required to be undertaken by all those involved in the lac trade to achieve goal of enhancing lac productivity, production, raw material or process product quality export, reduced cost, diversified uses, domestic consumption, employment and provide assured source of livelihood to resource poor population of sub-hilly tracts of different states of the country described above.

The lac industry is of great importance to India not only that it earns valuable foreign exchange, but it provides employment to a considerable number of people, e.g cultivators; middlemen, processors, brokers, exporters, product manufacturers etc. Any government or quasi-government intervention to stabilize lac prices can ease out fluctuations in prices of raw material as well as processed products. It would augment continuous demand of the product by the users, who, at times of high price, start looking for other alternatives. It is hopefully envisaged that in the coming years, lac cultivation and processing would generate enough employment to unemployed tribal youth and women at village level, ensuring livelihood support to lac-growers and others associated with lac trade.

Trends in export of various grades of processed lac from the country, over the past decade are indicative of increase in value-added products. It is hoped that in future value-addition of lac products will be maximized so that these products can be directly consumed by the user industry. The products, which need focus, are dewaxed decolourized food grade lac, bleached lac, aleuritic acid, isoambrettolide, lac dye and lac wax. More stress also needs to be laid on quality standardization and certification of these products.

Processing technologies would have to be upgraded to improve economics and quality of finished products. It is also envisaged that ultimately consumption of lac-derived products will be in specialty areas unrivalled by synthetic substitutes. They would include food, cosmetics, pharmaceuticals, varnishes and paints etc. Research efforts in development of products/applications in these areas would be more fruitful.

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2

Processing of Lac

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LAC encrustations on twigs of host-trees are removed by scrapping either manually or by machines. Lac resin, thus, obtained, is known as stick-lac. It contains a number of non-resinous impurities like wood particles, insect body, wax and dye, which are to be removed, refined and converted into commercially acceptable form, known as shellac. A number of methods have been evolved over the years to process raw lac as well as for extracting its minor constituents/by-products (Mukhopadhyay and Muthana, 1962).

The process of purification of lac, in general, consists of two steps: (*i*) washing of stick-lac or raw lac to remove sand and wood chips and drying of resin. This semi-refined form is called seedlac; (*ii*) The pure resin, shellac, is then obtained by hot filtration, either by the country (*bhatta*) process or in mechanized factories. Shellac obtained/processed in mechanized factories is called machine made shellac.

Improved methods of washing

Thakur (1937) made an exhaustive study into various aspects of washing of stick-lac and reported that addition of sodium carbonate or sodium silicate during washing improved colour and bleach index of seedlac, but decreased its yield. The use of 2% solution of potash alum, however, showed reasonable washing efficiency and did not have any corrosive action on seedlac grains. As the price of seedlac depends upon its bleach index (low bleach index product fetches higher market price) and a mixture of caustic soda and borax (1:5) and 0.6% on the weight of stick-lac was effective washing aid for producing light-coloured seedlac (Ghosh and Bhowmik, 1957). Soaking seedlac overnight in 0.25% aqueous solution of ammonium oxalate, followed by one wash with 0.125% solution of the same has also been observed to reduce bleach index by about 20.

Similarly, sodium perborate (0.6% *w/w*) was reported to be a good washing aid and effective in reducing colour of seedlac, but was not cost-effective. Ghosh and Bhowmik (1957) also studied role of reagents

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including ammonia, sodium sulphite, potassium permanganate, bleaching powder, potassium dichromate and hydrogen peroxide and noted advantages and disadvantages of each. It was, however, generally accepted that potassium permanganate (0.1% on the weight of stick-lac) is the most satisfactory washing aid, although seedlac needs a final wash with dilute sulphuric acid to remove brownish tinge imparted by potassium permanganate. According to Ghosh and Sengupta (1974) maximum improvement in colour and other properties, *viz.*, gloss, heat polymerisation time (HPT) and flow occurred upon addition of 0.1% oxalic acid on the weight of stick-lac. Out of the various synthetic detergents available in the market, *Genteel* was found to give optimum results (Table 2.1) during conversion of stick-lac to seedlac (Banerjee and Ghosh, 1979-80).

Table 2.1. Effect of various washing aids on the quality of seedlac

Washing aid	Quantity used (%) on stick-lac	Properties of seedlac		
		Average yield (%)	Colour index	Bleach index
Control	-	66	19	121
Washing soda	0.1	60	15	95
Borax + NaOH (5:1)	0.6	60	14	82
$KMnO_4$ followed by H_2SO_4	0.1	65	16	98
Commercial detergent (*Genteel*)	0.1	63	14	86

Hand-made seedlac grades commonly available in the market are: (i) Ordinary/genuine *bysakhi,* (ii) Fine *bysakhi,* (iii) Golden *bysakhi,* (iv) Golden *kusmi,* (v) Golden *bysakhi* – bold grain, (vi) Golden *kusmi* – bold grain, (vii) Golden *kusmi* seedlac – medium and (viii) Manbhum fine seedlac (*baisakhi* crop is commonly referred to as *bysacki* or *bysakhi* in the lac trade).

Conversion of Seedlac into Shellac: the Bhatta Process

The indigenous method of making shellac from seedlac is popularly known as country process or *bhatta* process. In this, a long sausage-shaped cloth-bag, usually 10 m long and 5 to 7.5 cm in dia, is tightly packed with seedlac with the aid of an iron funnel (*bharna*). The filled-in-bag is held at the end near a specially designed wood charcoal hearth or *bhatta* by a *karigar* or melter. The oven is typically designed with vertical walls on three sides and an arched roof. The other end of the cloth-bag is tied to the axel of a windlass or *charkha,* and is continuously twisted by another worker (*pheraiya*). Molten lac resin and wax oozes out of the cloth bag, which acts as the filter, by the twisting pressure. The *karigar* scrapes off molten lac from the surface of the bag with a spatula or *korni* and drops it onto a stone slab (*dongi pathar*) in front of the oven, which is previously wetted with hot-water. When the quantity of the molten lac is sufficient to form a sheet, it is scooped off, mixed well and again put on the surface of the cloth-bag to ensure a uniform, viscous melt mix. A sufficient amount of the well- basted resin is eventually scraped off by the *karigar* and transferred onto the glazed surface of a ceramic jar (*pipa*), filled with hot-water. *Bhilwaya* or stretcher spreads the plastic lac as a sheet on the *pipa's* surface with a palm leaf. The stretcher then peels off molten mass from the surface of the *pipa* and gradually stretches it by using his feet, both hands and teeth in front of the radiant heat of the *bhatta*. A plastic, semi-transparent thin sheet is thus obtained. Sometimes, two stretchers can be involved in this process to make a larger sheet. The entire process of melting and stretching requires considerable expertise and experience on the part of the component workers. The stretched sheet is cooled by laying flat, away from oven, after which, it is broken down into small flakes of shellac (colloquial: *chapra)*. Sometimes, instead of stretching into thin sheets, the molten resin is simply dropped as small blobs on galvanized iron sheets or *khola,* on which it spreads into small discs called button lac. The manufacturers' stamp can also be embossed on these buttons while they are still in a semi-plastic condition. Refined lac is commercially marketed both as shellac as well as button lac.

The cloth bag can be cleaned after recovery of shellac and reused 3- to 4-fold. The resinous material along with impurities present within the bag is called *kiri*. Sometimes, resin is mixed with old seedlac to facilitate melting process. In general, *kusmi* seedlac gives higher yield than *rangeeni* grades. Similarly, *baisakhi* seedlac is reported to give better yield than *katki* seedlac. The following grades of hand-made shellac are available in the market: (a) lemon one, (b) lemon two, (c) standard one (d) superior lemon, (e) superior *kusmi* lemon, (f) *kusmi* button lac, (g) superior *kusmi* button lac, (h) light pure button lac, and (i) pure one button lac.

Machine-made shellac

This is manufactured either by heat process or by solvent process. In a typical mechanized lac factory, stick-lac is first fed into a series of rollers for crushing before being transferred to charging tanks, where lac particles are soaked in water for about an hour. The soaked raw material is then fed into cylindrical washing barrels, fitted with centrally rotating stirrers and 60 mesh screens on the sides, which are protected by perforated iron plates. The washing is continued until almost all water-soluble lac dye flows out of screens. The washed seedlac is then discharged from washing barrel into a series of centrifugal machines, which remove the free water adhering to seedlac grains. The damp seedlac is then transferred to a drier for drying. The lac wash water is collected in tanks and filtered through fine cloth to remove the finer particles of lac resin or *molamma.*

Manufacturing machine-made shellac by Autoclave process

Seedlac is spread on a series of circular brass sieves (20 to 24 mesh), each sieve being placed over a metal funnel having a central draining system. Several such units are fitted in a frame in an autoclave, having heating arrangements and designed to facilitate removal of filtered lac periodically. The autoclave generally operates at steam pressures of 3 to 4 kg/cm^2 and purification of lac usually takes 2 hr/batch. The refined, fused lac, coming out of the autoclave contains up to 20% moisture. Hence, it is collected in shallow, steam-heated pans to allow moisture to escape. The lac is then transferred to steam-heated flaking rollers. Shellac flaking out of these rollers is stretched mechanically or by hand. Machine-made shellac is somewhat opalescent (due to occluded air bubbles) than hand-made shellac. However, autoclave shellac compares favourably with hand-made shellac in almost all aspects and also has comparatively less wax content (2 to 3%) when compared with *bhatta* shellac (4.5 to 5.5%), which is intermediate, in wax content, between dewaxed lac and hand-made shellac. This is because *kiri* remains within autoclave, retaining a large proportion of wax. The autoclave method is particularly suitable for small-scale industries. Other salient features of the autoclave method is that the rate of production is higher than the *bhatta* process and cost of production is about 50% lesser than the former.

Shellac can also be reclaimed from old seedlac by autoclave process. However, yield of *kiri* is more and life and flow of machine-made (MM) shellac are lower as compared to hand-made shellac. Moreover, colour of MM shellac is darker than *bhatta* shellac. It is reported that the flow and colour of MM shellac can be improved by smearing seedlac with formalin and by treating molten lac with a small quantities of oxalic acid.

Shellac directly from stick-lac

The entire process of washing of stick-lac, either in stone vats or washing barrels, followed by production of shellac by country process or solvent method or by an autoclave results in several by-products, *viz*., *molamma, ghonghi, kiri* etc. The loss of lac resin has been estimated to be 25%. Ghosh and Sengupta (1976) extracted stick-lac with rectified spirit and with acetone and recovered resin either by distilling of solvent or by precipitating resin with 1% aqueous salt solution. In the process, stick-lac is crushed to 8–10 mesh and agitated with 94 to 95% alcohol (7 litres/kg of resin content in stick-lac) at room temperature for 4 hr. Commercial acetone can also be used at 40°C. The extract is filtered through drill-cloth or filter-press and residue washed with fresh solvent (1litre/kg). The filtrate may be decolourised with *Norrit* and a few drops of acetic acid, followed by precipitation with efficient stirring, using 1% aqueous sodium chloride (NaCl). Alternatively, 50 to 60% of solvent may be recovered from the filtrate under low pressure and the residual material is poured into salt solution. The lac resin eventually settles down as a spongy mass (precipitated lac), which is washed with water, dried and kept in boiling water for 15 to 20 min to remove last traces of solvent and water solubles. The material may then be cooked on steam-heated pans and then drawn into sheets. Although colour of the shellac may be somewhat darker, use of 8 to 10% activated charcoal (on the weight of lac) for *rangeeni* stick-lac and 4 to 5% for *kusmi* stick-lac results in shellac, which is identical to *bhatta* shellac. These shellacs also have better life under heat and flow as compared to *bhatta* shellac or autoclave shellac.

The residue left over from solvent extraction of stick-lac contains wax and dye in addition to insect debris and other insolubles. The wax (20 to 25%) and dye (4%) on the weight of residue can easily be extracted with *n*-hexane and water respectively. The process does not produce insoluble by-product like *kiri* and no objectionable effluents from factory premises.

Dewaxed lac manufacture

Demand of dewaxed lac is greater in western countries, as it produces clear varnishes and brighter films, having superior adhesion. Besides, absence of wax in lac facilitates manufacture of value-added products through chemical modifications etc. Dewaxing can be carried out using organic solvents (Cassard, 1913; McCullock, 1937; Annon. 1942; and Bhowmik 1946) or in aqueous medium (De 1945; Gidvani and Kamath 1945; and Khanna and Sankaranarayanan, 1962). Dewaxing of lac is usually done by dissolving it in cold alcohol (optimum 10%), in which wax is insoluble, filtering to separate wax and reclaiming lac after distilling of solvent. The method requires a solvent recovery plant and the process is somewhat tricky as there are always chances of charring/polymerization of lac during distillation, unless the process is carefully monitored. The final product, however, contains about 0.5% alcohol, thus, making it susceptible to blocking during hot weather (Banerjee and Khanna, 1974).

Bhowmik (1946) suggested another method, involving digestion of seedlac in kerosene oil at 45° to 50°C for about 1 hr. In the process, seedlac retains all desirable properties, including grain size. However, only wax present on the surface of the grains is removed and the wax present within the grains remains within; thus, the product contains about 3% wax.

Since lac wax is insoluble in alkali, Gidvani and Kamath (1945) attempted preparation of dewaxed lac by dissolving seedlac in alkaline solution and removing wax by filtration. The lac resin is subsequently precipitated by addition of acid to the filtrate. The dewaxed lac obtained by this method is darker than parent seedlac. De (1945) attempted to prepare dewaxed lac in aqueous sodium carbonate solution after partial bleaching. It was observed that addition of bleach liquor facilitated coagulation of wax and its separation. This method is a three-step process and partially bleached lac containing about 1% wax is obtained.

Banerjee and Khanna (1974) suggested a simpler method for preparation of dewaxed lac in aqueous medium. In this method, about 10% (w/w) of lac wax is added to lac solution, which is heated to boiling temperature to make an intimate mixture of all waxes present in the solution, which is subsequently cooled. Most of the wax present forms a hard mass, floats on the top and can be removed easily. The optimum concentration of lac is 10%, temperature is 10 ± 2°C and time is 1 hr. The solution portion is taken out from the bottom of the vessel and filtered. Kieselguhr (5% on the weight of lac) and rayon were found efficient filtering aid and filtering medium respectively to remove last traces of wax. Dilute sulphuric acid (10%) is added to filtrate to reclaim dewaxed lac. The precipitated lac is washed free from acid and dried. The end product has less than 0.2% wax.

Improvement of dewaxing technique in aqueous medium

Dewaxing of lac in aqueous medium generally takes about 48 hr. Ghosh (1981-82) reported a method in which dewaxing can be done within 20 to 24 hr. The method involves dissolving seedlac (1kg, 10 mesh) in water (3:1 w/v) containing sodium carbonate (80g) and sodium sulphite (30g) at 80° to 85°C for 45 min. and filtering solution through muslin-cloth. The filtrate is cooled down to 15° to 16°C. Cellulose powder (70g) is then added, mixed thoroughly and filtered through a cloth. Sodium hydrosulphite is added to the filtrate for obtaining normal colour of shellac. Lac is then precipitated from the filtrate by the addition of 5% H_2SO_4 and subsequent washing with requisite amount of water. The cellulose powder and residue obtained from seedlac solution are hot extracted with *n*-hexane to recover wax. The dewaxed shellac obtained by this method has been reported to contain an average of 0.12 to 0.16 % wax. The method was found reproducible even up to semi-pilot scale (10 kg/charge).

Shellac and dewaxed lac manufacturing in aqueous medium

As already described above, shellac can be prepared from seedlac by heat process and dewaxed lac can be processed by solvent process. Ghosh *et al.* (1979–80) prepared both types of lac in aqueous medium, thereby eliminating by-products like, *kiri* and *passewa*. On an average, life, flow and colour of regular shellac were found to be 36 to 38 min. 47 to 49 mm and 11 to 12.5 respectively; the corresponding values of parent seedlac were 44 to 46 min, 45 to 48 mm and 13.5 to 14 respectively. The wax content of the dewaxed lac was found 0.12 to 0.14 %. The performance of the dewaxed lac prepared by this method was comparable with that of autoclave shellac/ dewaxed lac obtained by solvent process, when used in several shellac-based formulations (except in manufacturing of shellac etch primer, the product gelled).

Dewaxing of lac in solvents other than spirit

Attempts were also made to use isopropyl alcohol in place of denatured alcohol for dewaxed lac manufacturing in solvent medium (Banerjee and Khanna, 1973). It was observed that the product obtained in this manner had lighter colour with life under heat and flow of the same order as that obtained from conventional method, *i.e.*, using denatured spirit. Yield was, however, lower (~ 70%) compared to that obtained by usual method (~ 85%).

Dewaxed decolourised lac manufacture

Dewaxed decolourized lac is in demand in different industrial applications, especially, for coating tablets, confectioneries etc. Dewaxing can be done by usual process and for manufacture of decolourised lac, pure and dry grade of activated carbon was found quite effective. Banerjee (1988) made efforts to improve the process of dewaxing and decolourizing of seedlac by using various concentrations of alcohol (70 to 98%) at different temperatures. It was reported (Banerjee, 1985) that use of 98% alcohol produced 82% yield of lac resin with wax content of 0.18% and colour index of 0.70 at 11° to 14°C. Wax content could be reduced to 0.14% with the use of 70% alcohol at 11° to 18°C, but yield was reduced from 82 to 85% to 22 to 25%, with an increase in colour index from 0.7 to 1.3. Banerjee (1988) discussed different grades of activated carbon. Attempts were further made (Banerjee, 1985) on the preparation of dewaxed decolourized lac using different solvents. Rectified spirit, distilled denatured alcohol and methanol were found suitable for yield, colour index and wax content. Isopropanol and acetone were reported unsuitable as yields of the end products were quite low.

Dewaxed decolourized lac possessing very good life (118 min.), flow (180 sec) and colour index (0.45) has been reported (Annon. 1954-55). Acid value (117.2) was, however, quite high when compared with parent lac (73). Some of the precautions (Mukhopadhaya and Muthana, 1962) to be taken for manufacturing of dewaxed decolourized lac are as follows:

- Filtration is the key problem in manufacturing dewaxed decolourised lac. Filtration becomes progressively difficult, if the mixture is vigorously agitated during dissolution or kept too long in contact with spirit before filtration. Large grains of seedlac should be broken, and by-products e.g., *kiri* etc. should be sieved out through 10 mesh. The time of dissolution should be 1 hr with slow stirring. It may suitably be extended to 2.5 hr for old or slowly dissolving seedlac.
- Alcohol should be cooled down to 18°C before dissolving seedlac and temperature should be maintained throughout the operation.
- A steady and slowly increasing pressure enables efficient filtration.

- The residue in the filter press is washed with strong spirit only and washings can be mixed with the filtrate.
- The filtrate is either heated to recover alcohol or passed into storage tanks for decolourisation for manufacture of various grades.

Bleached lac manufacture

Bleached lac has a constant demand in western markets. Nearly 50% of the world consumption of lac is in the form of bleached lac or white lac. Although laccaic acid (lac dye) is removed during processing of stick-lac into shellac, the erythrolaccin (tetrahydoxyanthraquinone), which is insoluble in water and present in intimate combination with resin, is not removed and it is this group of pigments that impart characteristic amber colour to shellac. This colour can be removed by bleaching.

Until recently, India did not have any large-scale bleached lac-manufacturing unit and all bleached lac was manufactured in United Kingdom, Germany and the USA. However, during the last few years, bleached lac is manufactured on a large-scale in India and is exported. A number of methods for bleaching of lac are available (Venugopalan, 1927; Murty, 1933; Gibson, 1934; Hituki, 1935; Faucett, 1937; Murty, 1939; Gidvani and. Kamath, 1946; Baba, 1946; Takahashi, 1950; Ubukata, 1954; Khanna, 1963; and Khanna and Sankara-narayanan, 1962, 1965), but most commercially adopted method involves bleaching with sodium hypochlorite. In bleaching process (Khanna, 1970), 10 parts of seedlac or shellac is treated with 40 parts of water containing 1 part of anhydrous sodium carbonate with efficient stirring. The temperature is maintained at 85° to 90°C for 30 min. The hot extract is passed through a brass sieve (100 mesh) and insoluble is washed out with hot water. The filtrate is diluted to 20% solid content and bleaching is carried out at 25±1°C. Bleach liquor is prepared by passing chlorine through an ice cold, 1.5 N solution of commercial NaOH, caustic soda, the strength of which is adjusted to 3±0.05% and free alkalinity to 0.02–0.04 N (pH 11.0–11.2). The bleach liquor is added in small installments. The solution is then cooled to 20°C and diluted. The bleached lac is reclaimed by slowly adding 5% sulphuric acid in a thin stream to the above solution, followed by agitation for 10 min to ensure complete precipitation. The precipitated bleached lac is then washed thoroughly with cold water (< 20°C) to free it from sulphates. The product is dried in shade to a moisture content of ~2%. Murty (1939) reported that acetic acid (CH_3COOH) was better for precipitation step as compared to inorganic acids like HCl and H_2SO_4, especially as regards to solubility of the end product. However, study was not made on the cost effectiveness of the process.

During preparation of wax-free bleached lac, last traces of wax can be removed by extracting solution of seedlac in soda with white spirit at 90°C for about 20 min (Khanna and.Sankaranarayanan, 1962). Wax-free solution of bleached lac gives clearer solution in alcohol as compared to that obtained by conventional cloth-filtration method. The yield of the product was higher by 3 to 5%. During bleaching process, it is believed that carboxyl group of lac reacts with aqueous sodium carbonate to form sodium salt of lac. The action of sodium hypochlorite can be explained by the following reactions (Khanna, 1970):

$$NaOCl \rightarrow NaCl + O$$

$$NaOCl \rightarrow HOCl + NaOH$$

$$HOCl \rightarrow HCl + O$$

$$HOCl \rightarrow Cl_2 + H_2O$$

Previous workers expected that during bleaching, lac resin undergoes various reactions e.g., oxidation, chlorination (by addition and substitution) and hydrolysis due to the evolution of oxygen, chlorine and sodium hydroxide. It was also postulated that oxidation of hydroxyl groups to carbonyl groups and possibly rupture of chain itself at the site of the vicinal hydroxyl groups to yield water-soluble products (Khanna, 1970). The free alcohol of the bleach liquor and also the alkali that is produced during bleaching partially hydrolyses resin, resulting in an increase in free acidity.

Properties of bleached lac

Life under heat (at 150^0C) and fluidity of lac are adversely affected, even if the resin is precipitated from a solution of aqueous sodium carbonate without bleaching. Addition of bleach liquor causes further deterioration. However, a minimum of 10 to 12 min of life under heat was found for all samples of bleached lac, irrespective of the type of lac used. Yield (93.7%) and acid value (71.5) of bleached lac obtained with bleach liquor of free alkalinity 0.04 N, decreased to 87 and 74.8 respectively for increasing alkalinity of bleach liquor to 0.34 N. Khanna (1970) reported that change in intrinsic viscosity in bleached lac than parent lac. Bleaching also caused deterioration in the keeping quality (alcohol solubility) and a progressive deterioration was noticed with increase in bleach liquor *i.e.*, amount of chlorine present in bleached lac. No molecular complexity of the resin has however been reported. The absorption spectra studied in the ultraviolet and visible region (Goswami *et al.*, 1981) for bleached lac revealed absence of absorption maximum at 425 nm, which is characteristic of the pigment present in the lac resin at that wavelength.

Storage of bleached lac

The main drawback associated with bleached lac is its poor keeping quality. The solubility of the material falls rapidly and material soon becomes unfit for use. Murty (1939) recommended cold storage (~10°C) of bleached lac to ensure longer life. Films prepared from old bleached lac takes longer period for drying. A reduction in acid value of bleached lac varnish was also observed on storage, which was attributed to the formation of esters between alcohols (solvent) and acid present in bleached lac. Murty (1939) further suggested that formation of methyl esters was plausible. Bleached lac varnish, even when stored in glass containers at room temperatures changes colour from yellow to red. Such varnishes when stored at lower temperature (10°C) retained the original colour. Bleached lac in the varnish form can be stored for a longer period, if eompared with solid form. Washing of bleached lac during its preparation plays an important role in its final quality. Wolff (1916) opined that gradual insolubility developed in bleached lac is due to mineral acids, which were not removed completely during washing. Use of boiling water for washing was detrimental to life of bleached lac (Murty, 1939). Precipitating bleached lac as granules and washing with cold water retained its solubility over a longer period and possessed whiter appearance.

Lead thiosulphate was found efficient stabiliser for bleached lac (Khanna and Sankarnarayanan, 1962). Storage life of the material with stabiliser under heat was found twice than without stabiliser. No increase in insolubility was noticed for storage under laboratory conditions for 1 year. Even under adverse conditions of storage (45 ±1°C up to 240 hr), the increase in insoluble was noted to be 1/3rd of that of the material without the stabiliser. The poor storage stability of bleached lac has been attributed to the combined chlorine (1 to 3.5%) usually present. This chlorine is believed to split off gradually in hydrochloric acid, which results in insolubility of the resin in alcohol. Mulani and Watson (1926) although reported improvement in keeping quality with sodium thiosulphate, Khanna and Sankarnarayanan (1962) contradicted their observations. Flat discs of various samples were irradiated with ultraviolet rays from a quartz mercury vapour lamp for about 50 hr. Exposed surfaces turned brown when compared with colour of undersurfaces or with control. Samples which had undergone hydrolysis and dechlorination during bleaching operation were more drastically affected as compared to control surfaces.

Bleached lac has been reported to have better storage life when stored under water (Nagel *et al.*, 1927) due to the fact that any hydrochloric acid which may split off would be sufficiently diluted to become innocuous, but improperly prepared bleached lac becomes insoluble after a period of time even when stored under water. Any free chlorine present in bleached lac has been found to have a harmful effect on its keeping quality (Murty, 1939) and thus the use of antichlors has been recommended after completion of the bleaching step. However, Murty (1939) showed that neither the presence of free chlorine nor its removal with antichlors, seemed to have any effect on the keeping quality of bleached lac. Murty *et al.*(1939)

observed that the main factors determining the bleachability of seedlac were actually the quantity of animal matter present; since the colouring matter laccaic acid and nitrogen are derived from the same source *viz.*, the remains of lac insects. Thus, lesser the colour index of seedlac, better will be the bleachability of the seedlac. *Kusmi* and *khair* seedlacs produced best bleaching grades compared to *ber* and *palas* seedlacs. Bleaching quality was also adversely affected for polymerized lac (stick-lac which tends to block). It was reported that coarsely ground lacs required considerably less bleach than finely ground ones (Murty, 1939).

Determination of bleach index

The quantity of bleach liquor required for satisfactory bleaching of any lac sample can be calculated from its bleach index. Lac samples are treated with bleach liquor to achieve complete bleaching and the volume of the bleach liquor is noted. Sankaranarayanan and Bose (1954) developed a method, in which same amount of bleach liquor was added to all samples of lac and the degree of bleaching affected in each case was determined from the colour of bleached solution (free from wax) in terms of N/1000 iodine. The advantages of the method over the existing one were: (i) no standard seedlac was required, (ii) repeated additions of small quantities of bleach liquor and repeated filtrations and testing were avoided, and (iii) different procedural details for different grades of lac were also eliminated. The results obtained were independent of moderate variations in laboratory temperatures. Later, Khanna and Sankaranarayanan (1956) and Chopra and Sankaranarayanan (1962) made further improvements in the determination of bleach index of lac using Klett Sommerson photoelectric colorimeter. A direct relationship could be established between observed deflections in the colorimeter and bleach indices of the samples. The method was claimed to be convenient over the previous method due to (i) all personal error in colour adjustments could be avoided, (ii) elimination of eye fatigue which usually resulted when a number of determinations were to be carried out, and (iii) no need to prepare iodine standard from time-to-time once the colorimeter was calibrated.

Alternative bleaching methods

Mylor (1931) attempted electrolytic methods for bleaching an alkaline solution of lac, using sodium chloride, with or without sodium fluoride as an electrolyte. Seisakujo (Jap pat.) carried out electrolysis in a dilute solution (10%) of shellac in Na_2CO_3, NaOH, NaCl system and the bleaching was completed within 8 to 16 hr. He recommended a current density of 0.005 – 0.01 amp/cm^2 and temperature below 70°C. It is, however, not known whether electrolytic bleaching is used commercially.

Gidvani and Kamath (1946) recommended gaseous chlorine instead of aqueous hypochlorite. Bleaching is best carried out with gaseous chlorine at pH 8±0.5. The process was stated to be economical. Bleaching of lac with sodium chlorite was also attempted at Mathison Alkali Works (1946). Bleaching with chlorite can also be carried out in a water miscible organic solvent system such as 95% ethyl alcohol along with an antichlor (H_2O_2). Sengupta (*op. cit.* Mukhopadhyay and Muthana, 1962) modified the method of hypochlorite bleaching of lac, which was less time-consuming and required much bleach liquor. The yield and properties of the bleached lac were reported similar to those obtained by conventional method, excepting that chlorine content and acid value of the product were low.

Prasad and Khanna (1974) used a combination of sodium hypochlorite and hydrogen peroxide as bleaching agent instead of the former alone, as it adversely affected desirable properties of the end product, *viz.*, life under heat, flow and keeping quality due to entry of chlorine in the lac molecules. The product thus obtained possessed satisfactory colour, good storage stability and flow behavior, similar to those of commercial dewaxed lacs. The chlorine content was lower (0.4%) as against conventional bleached lac (1.5%).

Mishra and Khanna (1975) developed a method in which a considerable reduction in bleaching time (4 hr) was achieved when compared with conventional method (24 hr). A substantial saving in bleach liquor consumption was also reported. In this method, bleaching is done in fine suspension form (in contrast to solution form). A mixture of hydrogen peroxide and sodium hypochlorite was also used as bleaching agent instead of latter alone. This process yielded a product with 20 to 25% chlorine content.

A method of preparation of bleached lac was developed from *molamma*, by slight modification of the conventional method *i.e.*, by carrying out the initial alkali extraction at a low temperature (50°C) for 4 hr (Ghosh and Sengupta, 1967). The bleached lac obtained by this method was reported to be comparable in all aspects with that obtained from seedlac by conventional method and also possessed better storage stability. Bleached lac is sold as *hanks*, due to poor keeping quality, particularly when it is intended for use in aqueous varnishes or emulsions. It is also sold as a coarse white powder in the name of 'bone-dry' shellac or 'vac-dry'. Further, there are two types in each of the above forms *viz.*, (a) regular bleached lac (cloudy or waxy), and (b) refined bleached lac (transparent or wax-free).

Byproducts of the lac industry

During the processing of stick-lac into seedlac and then seedlac to shellac, certain valuable byproducts are obtained. They contain a good amount of lac resin. Several methods have been developed for the utilization of these by-products. The main byproducts are *molamma, kiri, passewa* etc. (IS: 2978 – 1986; IS: 4908 – 1968). These are also exported at a comparatively lower price than seedlac and shellac.

Molamma. These are fine grains of washed lac (seedlac). There are two types of *molamma* available in the industry. As per IS:2978-1986, the minimum and maximum lac resin content should be as given in Table 2.2.

Table 2.2. Lac resin content in *Molamma.*

Type	Lac content	
	Minimum	Maximum
Molamma special	80	85
Molamma I	70	< 80

Kiri. The solid mass, remaining within filter press in machine made process or within cloth bag of country process (for the production of shellac from seedlac), is known as *Kiri.* It contains 30 to 65% lac resin besides other impurities. Attempts were made over the years to extract lac resin from *kiri*, either by alcohol or aqueous alkali. The life, flow and acid values of lac resin recovered by the solvent process and aqueous alkali were 20 min, 17 min, 85 and 19 min, 16 min and 91 respectively. Thus, parameters such as life and flow of lac resin recovered from *kiri* are inferior to those of shellac. The acid value of the recovered resin is, however, higher than shellac. There are three varieties of *kiri* available commercially. As per IS: 2978 (1986) specifications, the varieties of *kiri* can be graded as shown in Table 2.3.

Table 2.3. Lac resin content in *Kiri.*

Grade	Resin content (min) %	Resin content (max) %
Kiri I	55	65
Kiri II	40	<55
Kiri III	30	<40

There is no regulation, however, for colour index. This property is to be agreed upon solely between the purchaser and the manufacturer. Lac reclaimed from *kiri*, normally by solvent process, is darker and is known as *garnet lac.* It finds use in cheaper applications where colour does not have much relevance.

Passewa. The small quantity of lac which remains adhered to used cloth-bag during hot filtration of lac resin (country process) is removed by boiling the bag in water containing little alkali, where most of the resin melts and rises to water surface. It is then ladled out and pressed into cakes. The BIS specifications (IS: 2978 – 1986) for minimum lac resin content is 70%, there is no maximum limit. Besides the above, there are other minor byproducts of the lac processing industries, which contain good amount of lac resin. These are collected and used for manufacture of shellac. Some of these are (IS: 4908 – 1968) *khood*: fine, dusty lac obtained when stick-lac is sieved before being washed and *kunhi*: this is seedlac of very small grain size, obtained during winnowing in the country process of manufacture of seedlac. Mention also has to be made of the by-products *viz. pathi, ghonghi, agila, bhusi* and *rangabatti*. *Bhusi* is obtained at different stages of making seedlac and contains 2 to 15% of lac resin and fine particles of wood. Local manufacturers do not reclaim lac from *bhusi*, which is sometimes exported at a nominal price.

Lac dye and lac wax. The lac factory effluents contain considerable amounts of lac resin, wax and almost entire amount of water-soluble lac dye (laccaic acid). These are valuable products and find use in different industries. Researches have been carried out for reclamation of these, which augment the profits of lac-processing units. The institute has recently established a pilot plant for manufacture of technical grade of lac dye.

Hygienic disposal of lac factory effluents

The wash water originating from lac processing units, besides containing water soluble dye, also contains fragments of insect bodies, proteinacious matter derived from insect bodies, vegetable glue, some quantity of sugar etc. The effluents are generally collected in a pit outside the factory. The accumulated wastes starts putrefying within 24 hr owing to the presence of nitrogenous matter and the whole surroundings acquire an obnoxious smell. This environmental hazard is a severe problem for lac-factory owners. Bhowmik and Ghosh (1959) studied effect of 19 chemicals on wash-water, in an effort to do away with putrefaction. The study revealed that acids, lime, bleaching powder, creosote oil and copper sulphate could stop putrefaction. Sulphuric acid was chosen because it was the cheapest. It was further observed that addition of 0.1% sulphuric acid (on the total volume of wash water) was sufficient to arrest putrefaction. It also precipitated dye and other matters. While using sulphuric acid, no putrefaction was observed even after 12 days after application, whereas with the other acids, putrefaction commenced after 5 to 6 days. It is to be mentioned here that the precipitated material is a source of dye, wax etc., recovery of which has also been worked out by researchers. Furthermore, the residual water (after precipitation) can also be recycled for further washings.

Lac-mud

During washing of stick-lac to seedlac, the effluents of the lac factories are allowed to flow and collect in a reservoir. The reservoir may be cemented tanks or shallow pits, dug outside factories for this purpose. The accumulated wash water is treated with acid, precipitating all solid matter (popularly called lac-mud) and the clear water separates out. Yield of lac-mud is about 8% on the weight of stick-lac used. Lac-mud is also a source of lac dye and lac wax. Processes have been developed at the erstwhile Indian Lac Research Institute for reclaiming both lac dye and lac wax from lac-mud. Because of the organic matter content of lac-mud, its manurial value (Bhowmik, 1984-85 and Singh, 1989-90) was studied (Table 2.4).

Table 2.4. Manurial value of lac-mud than castor cake and farmyard manure

Materials	Organic matter (%)	N(%)	P_2O_5 (%)	K_2O (%)
Lac-mud with wax	38.8	2.8	0.4	1.3
Lac-mud (wax free)	42.7	4.7	0.6	1.6
Castor-cake	36.6	4.3	1.8	1.4
Farmyard manure	32.2	0.5	0.3	0.4

Wax-free lac-mud was recommended for soil application. Furthermore, since lac-mud contains lac resin, it was found to possess binding properties and the Soil Conservation Laboratory, Hazaribagh, reported that shellac also prevents soil erosion (Bhowmik, 1984-85).

Mechanisation of post-harvest operations

Efforts have been made at the Indian Institute of Natural Resins and Gums to reduce drudgery in the different labour intensive operations, like scrapping of resins from twigs, washing, grading and winnowing operations. A few machines have been developed (Prasad *et al.*, 2001 to 2008), which are easy to operate, gender friendly and are easily adaptable at village level by lac-growers for augmenting profit in the trade. These are: Pedal operated lac washing machine; Hand operated roller type lac scraper (capacity 5.7 kg/hr, weight 50 kg); Pedal operated roller type lac scraper (capacity 6 kg/hr, weight 55 kg; Power (0.25 HP single phase motor) operated roller type lac scraper: (capacity 10 kg/hr, weight 70 kg); Hand-operated lac grader (capacity 60 kg/hr); Hand operated lac winnower (capacity 500 kg/day compared to150 kg/day done by a woman labourer).

Small-scale lac processing unit: The unit comprises lac scraper-cum-crusher, lac washer, lac winnower and lac grader. The capacity of the unit is 100 kg/day. The cost of establishment is Rs 5 lakh and net profit of Rs 30,000 can be earned monthly.

Pilot plant for technical grade of preparation of lac-dye

A pilot plant has been set up at the then Indian Lac Research Institute for manufacture of 2 kg of technical grade of natural red colour lac dye from wash water of 400 kg stick-lac (Prasad, 2007). The yield of dye is about 0.17 to 0.31% by weight of stick-lac.

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3

Chemistry of Lac Resin and its Constituent Acids

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THE chemistry of lac resin is very complex and at the same time extremely fascinating (Bose *et al.*, 1963). Commendable results could only be achieved in the 1960s with the techniques such as column, paper, thin layer and gas-liquid chromatography, spectroscopic as well as conventional methods.

The resin on an average has five free hydroxyls, one free carboxyl, one aldehyde partly free and partly combined and a point of unsaturation, and linkages present are esters, acylal, acetal and ether. The oxidation of the resin with periodic acid (Sengupta, 1963) showed that one-thirds of the vicinal hydroxyl groups, in terms of aleuritic acid (a major constituent acid), is free and the rest are in combined form. The oxidation affords in aleuritic acid, w-hydroxyheptan-1-al and azelaic semi-aldehyde. But after oxidation (Sengupta, 1963 and Madhav *et al.,* 1967) of the resin no appreciable amount of either of the degradation products could be isolated. This suggested that most probably in this part of aleuritic acid, the carboxyl and the primarily hydroxyl groups are not free. The rest of the aleuritic acid appears linked up at least through one of the vicinal hydroxyl groups.

The resin is not a chemical entity and that it is composed of at least seven components (Sengupta, 1969) was made clear by its successful resolution into its components by thin layer chromatography over silica gel. It can be broadly resolved into 2 fractions by diethyl ether, an insoluble solid mass (~75%) called hard resin and a soluble soft mass (~25%) called soft resin. Sukh Dev and co-workers (Upadhye *et al.*, 1970 and Singh *et al.*, 1974) succeeded for the first time in isolating a few pure fractions by fractional precipitation from hard and soft resins. Sankaranarayanan and Kunhunny (1961-62) isolated a neutral fraction from soft resin, which was believed to be a lactone with 1 free hydroxyl group having empirical formula $C_{21}H_{37}O_3$. Later, Banerjee and Sengupta (1964-65) established that the neutral fraction, M.P. 49°C, is not a chemical entity but a mixture

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of at least 7 components. Prasad and Sengupta (1972, 1975) have fractionated hard resin into 6 fractions through the formation of urea-complexes. Few of these appeared to be essentially pure.

The constituent acids of the resin and its fractions fall under two categories: (i) hydroxy fatty acids, and (ii) hydroxy terpenic acids having the rare cedrene skeleton. The former was least soluble and the latter was highly soluble in water. The most successful method of isolation of these constituent acids is by alkaline hydrolysis. A certain portion of them was found present in uncombined state (Bose *et al.,* 1963). The investigators have taken either shellac, hard resin or its various fractions such as soft resin, pure and neutral fractions for study and the results obtained are described regarding isolation and characterisation of various constituent acids.

Aleuritic acid

This is readily obtained as sodium salt from alkaline hydrolysate. The acid (M.P. 100° to 101°C), was first isolated by Tschirch and Farner (*op. cit.* Bose *et al.,* 1963) and was characterized as *threo*-9,10,16-trihydroxy palmitic acid (I) by researchers. The structure was re-examined by Sengupta (1970) by chromatographic techniques after subjecting the acid to oxidation with periodic acid. The resulting acidic semi-aldehyde and the neutral semi-aldehyde after further oxidation and methylation were identified by GLC as dimethyl azelate and pimelate respectively, thus confirming the envisaged structure (I). The first conversion of the natural *threo*-acid to *erythro*-isomer (M.P. 126°C), was through the tribromo derivative (*op. cit.* Bose *et al.,* 1963). Madhav *et al.* (1964) prepared the same *erythro* isomer (M.P. 126° to 27°C), by chlorination of *threo* acid in acetic acid with hydrogen chloride at 110°C and hydroxylation of the chloro derivative. Chatterjea *et al.* (1976) prepared same *erythro* isomer by treating *threo* acid with concentrated hydrochloric acid at steam bath temperature followed by hydroxylation. Thin layer chromatography on boric acid impregnated plate (Sengupta, 1970; Morris, 1963 and Eswaran *et al.,* 1971) also confirmed the *threo*-form of the natural acid. Ames *et al.* (1961) demonstrated the *threo* form through transformation and conversion to various derivatives. Treatment of aleuritic acid (I) with phosphonium iodide, followed by alkaline hydrolysis, gave *trans*-16-hydroxyhexadec-9-enoic acid (III) which showed *trans*-HC=CH band at 970 cm^{-1}. Thus, the intermediate iodo-acetate (II) must be *erythro*-form and aleuritic acid is *threo*-isomer (I), since the formation of iodo-acetate involves an inversion.

In a similar manner treatment of aleuritic acid with hydrobromic acid and acetic acid gave the *erythro*-bromo-acetate (IV) which afforded the *erythro*-9,10,16-trihydroxyhexadecanoic acid (VI) on direct hydrolysis or through the intermediate 16-hydroxy-trans-9, 10-epoxy hexadecanoic acid

(V) and followed by further hydrolysis. This *threo*-form was further supported by the study of the infrared spectroscopy (Sengupta, 1970; Eswaran *et al.*, 1971 and Rao, 1967). The *threo*- acid showed two maxima at 1723cm^{-1} and 1656cm^{-1} while the *erythro*- acid only one at 1690 cm^{-1}. In the natural acid, the absence of absorption at 1690 cm^{-1}, which is characteristic of (=) stretching absorption of a dimeric carboxylic group, indicated that there is no dimer in *threo*- acid.

Eswaran *et al.* (1971) considered *erythro*-isomer exists predominantly in staggered conformation (VII) while *threo*-isomer in intramolecularly hydrogen bonded conformation (VIII) on the basis of NMR and IR studies. The use of polar solvents was found to produce marked effect on hydrogen bonding. Studies on the crystal and molecular structure of the *threo*- acid showed that in the crystal each aleuritic acid molecule has 7 hydrogen bonds linked to 6 different neighbouring molecules, 4 through vicinal OH groups and 3 through oxygen atoms of COOH and end OH groups, which proves that there is no dimer form and no intramolecular hydrogen bond present in the structure as suggested by Eswaran *et al.* (1971). Fig. 3.1

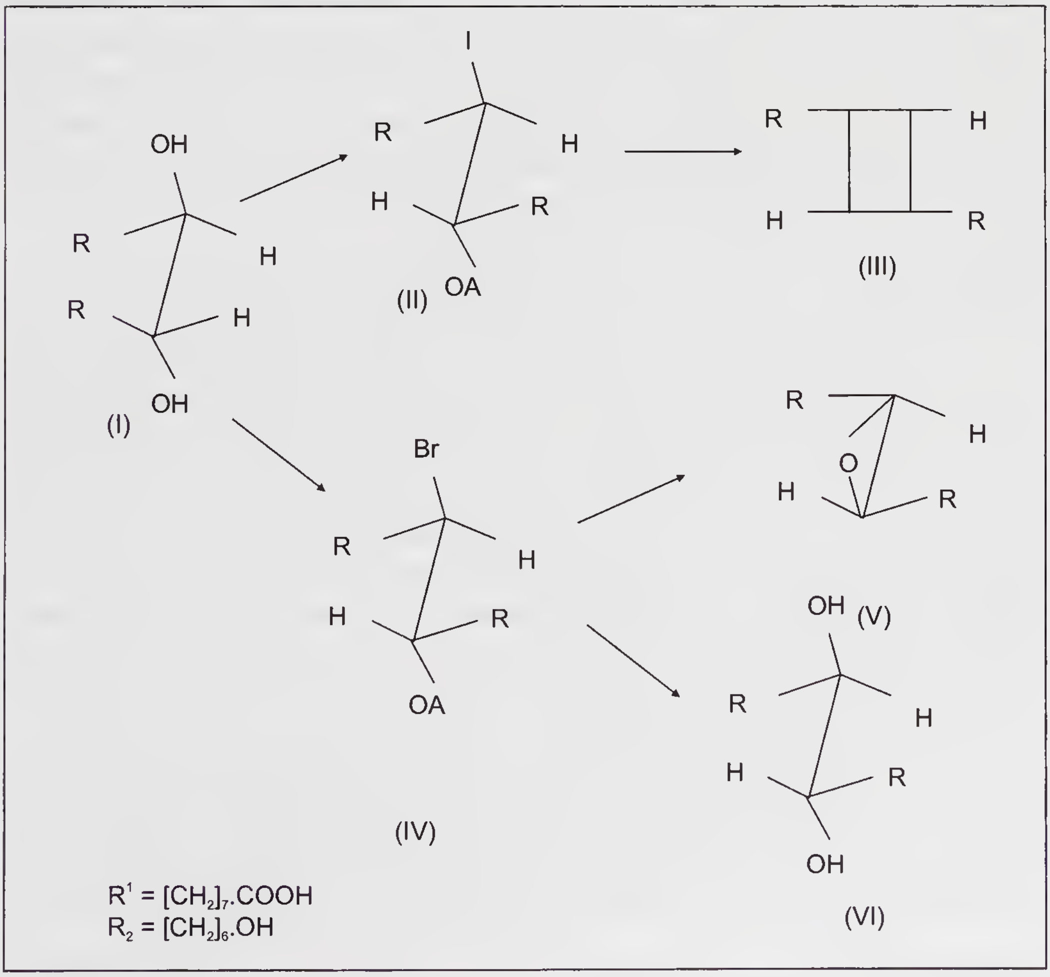


Fig. 3.1. Aleuritic acid formation as suggested by Eswaran *et al.*, 1971

There are two asymmetric carbon atoms at 9- and 10- positions in the molecule but the acid is always obtained in inactive form. Ames *et al.* (1961) noted a very small (+) rotation and considered that the acid may be either (+)-*threo* acid or a (±)-mixture containing more than 50% of the (+)-isomer. Eswaran *et al.* (1971) as well as Mc Ghie *et al.* (1971) and co-workers successfully resolved the natural acid into (+) and (-) forms through brucine and ephedrin salts. According to Eswaran *et al.* (1971) the (+)- and (-)-isomers had the same M.P. 102° to 103°C with rotation of [a] +27° and –30° while, McGhie *et al.* (1971) obtained M.P. 102.5 to 103 to 5°C and 103 to 104°C with [a] +24.65° and –24.45° respectively. *erythro*-Aleuritic acid (M.P. 125°C) was synthesized earlier by Mitter *et al.* (*op. cit.* Bose *et al.,* 1963). Baudart (*op. cit.* Bose *et al.,* 1963) also synthesized two isomeric aleuritic acids, M.P. 102 to 104°C. Ames *et al.* (1968) once again synthesised the *erythro* (M.P. 125°C) and (±)-threo (M.P. 99 to 101°C) aleuritic acids. Condensation of dilithio-derivative of oct-7-yn-1-ol with 8-bromooctanoic acid gave cis-16-hydroxyhexadec-9-enoic acid, which was semi-hydrogenated to 16-hydroxyhexadeca-9-enoic acid. cis- and trans-Hydroxylation then gave *erythro* and (±) *threo*-aleuritic acids respectively. The *erythro*-isomer from (+)-*threo*-acid was, however, found optically inactive (Chatterjea *et al.,* 1976). The isomers of aleuritic acid (Sengupta, 1970 and Rao, 1976) (M.P. 97° to 97.5°C and 93° to 94°C) were also found to be *threo*-9,10,16-trihydroxypalmitic acids. It may be said that either these are impure aleuritic acids or positional isomers with respect to all the 3-OH groups together.

Butolic acid

Butolic acid (M.P. 58 to 59°C), first isolated by Sengupta and Bose (*op. cit.* Bose *et al.,* 1963), was believed to be 6-hydroxypentadecanoic acid. Later, Christie *et al.* (1963) and Wadia *et al.* (1969) independently proved it to be (-) 6-hydroxytetradecanoic acid (methyl ester:$[a]^{19}_{D}$ –O-9° ; -2.2°). Christie *et al.* (1963) synthesised (+) 6-hydroxytatradecanoic acid (M.P. 65 to 66°C) from cyclopentanone and nonanoic acid by adaptation of enamine procedure. The (±)-acid has also been synthesized adopting 2 different routes by condensing: (*i*) ethyladipylchloride with dioctylcadmium, and (*ii*) cyclohexanone with octylmagnesium bromide and oxidizing the resulting compound. In both cases the ketoacid (X) (M.P. 69°-70°C) was obtained which after reduction afforded butolic acid (M.P. 61° to 62°C). From published data on hydroxy long chain fatty acids, all (-)-acids have R-configuration irrespective of chain length and position of OH group, Wadia *et al.* (1969) have tentatively assigned R-chirality for asymmetric centre for the natural acid (IX).

Minor acids

Christie *et al.*(1964) isolated and identified a number of acids, which are present in minor quantities in lac hydrolysate. These are tetra-, hexa- and octa- decenoic (XI) acids, 16-hydroxyhexadec-cis-9-enoic acid (XII), *threo*-9,10-dihydroxytetra-decanoic acid (XIII) and *threo*-9,10-dihydroxyhexadecanoic acid (XIV), Fig. 3.2a. The tetradecanoic acid was found to be a mixture of Δ^9 compound (~50%) along with significant amounts of Δ^4 and Δ^5 isomers and minor amounts of Δ^7 and Δ^8 isomers. The Δ^9 C_{16} and C_{18} acids were also accompanied with traces of Δ^7 isomers. There was also chromatographic evidence of a very small quantity of 14-hydroxytetradecanoic acid.

Aleuritic, butolic and all other non-hydroxy, hydroxy- and oxo-fatty acids except 9,10-dihydroxyhexadecanoic acid were isolated from soft resin by Agarwal *et al.* (1976). Another dihydroxy acid was also isolated which was confirmed to be 10,16-dihydroxyhexadecanoic acid (XV), Fig. 3.2a. All the above non- mono-, di- and tri-hydroxy acids along with the oxo-acid were found present in free state in shellac/seedlac (Sengupta, 1963-64) to the extent of nearly 6%.

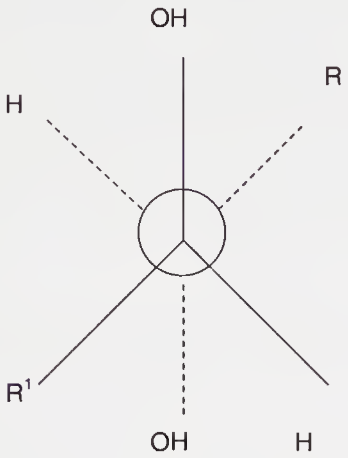
Shellolic and related acids

Shellolic acid was first isolated by Harries and Nagel (*op. cit.* Bose *et al.,* 1963) as its dimethyl ester (M.P 149°C). The acid melts at 206°C, is optically active $[\alpha]^{20}_D + 32.61$ and is an unsaturated dihydroxy dibasic hydroaromatic acid having molecular formula $C_{15}H_{20}O_6$. Yates and Field (1960) correctly proposed that it is a sesquiterpene with rare cedrene skelton (XVI). The spectrum of dimethyl shellolate showed that the double bond is configurated with the carboxylated ester group (IR: 2.9, 5.8-5.9, 6.11 μ; UV: λ_{max} 230 nm, å 6000) while NMR spectrum showed one vinylic hydrogen and one C-CH_3 group. Alkali fusion of the dimethyl ester afforded a lactonic diacid (XVII) (M.P. 199° to 201°C) as the major product with all the carbon atoms of shellolic acid. Dehydrogenation of XVII over palladium/charcoal and treatment of the resulting product with diazomethane gave the substitute coumarin (XVIII, M.P. 115° to 116°C). This coumarin was synthesised and spectra of both were identical. Based on the present and earlier observations a tentative relative configurational assignment for the acid was made by them (XVI), Fig. 3.2b; confirmed later by various investigators (Carruthers *et al.*, 1961; Cookson *et al.,* 1962 and Gabe 1962).

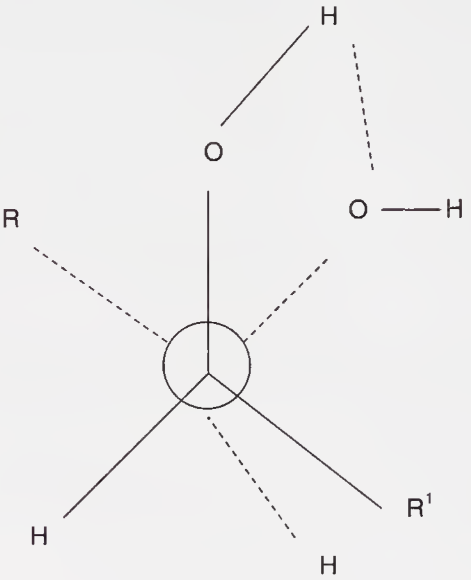
An isomer of shellolic acid (M.P. 232°-233°C) (decomposed); $[\alpha]_D$+49°) was also isolated (*op. cit.* Bose *et al.*, 1963, p.75) and may be similar to the one mentioned by Kirk *et al.* (*op. cit.* Bose *et al.,* 1963) with a melting point 238°C. It was later identified as the epimer of shellolic acid (XIX) Fig. 3.2b; and named epishellolic acid (*op. cit.* Bose *et al.,* 1963).

Jalaric acid

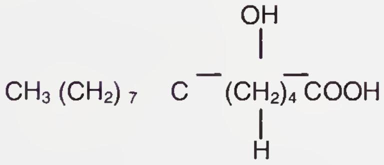
An aldehydic acid was isolated by Sengupta (1953 to 1955) from shellac



(VII)



(VIII)

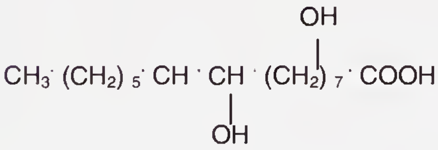


$CH_3(CH_2)_7\ \underset{H}{\overset{OH}{C}}-(CH_2)_4-COOH$ ...(IX)

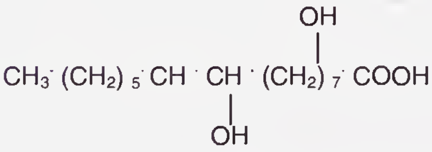
$CH_3\ (CH_2)_7CO\ (CH_2)_4\ COOH$ ... (X)

$CH_3\ CH_2\ (CH_2)_8\ (CH_2)_7 - COOH$ ... (XI)

$OH\ CH_2\ (CH_2)_5\ CH{=}CH\ (CH_2)_7\ COOH$ ... (XII)



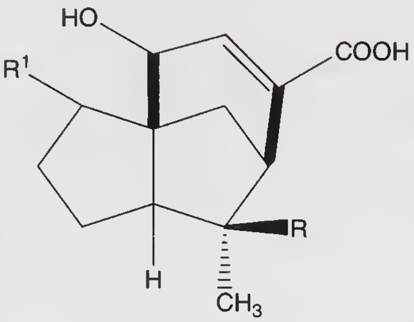
$CH_3\cdot(CH_2)_5\cdot CH\cdot \underset{OH}{CH}\cdot \overset{OH}{(CH_2)_7}\cdot COOH$ ... (XIII)

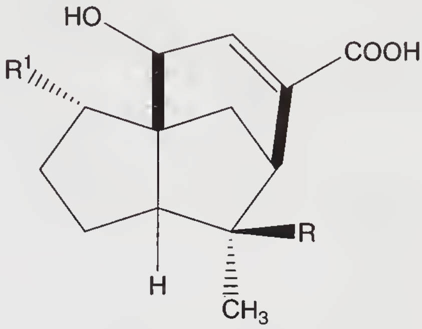


$CH_3\cdot(CH_2)_5\cdot CH\cdot \underset{OH}{CH}\cdot \overset{OH}{(CH_2)_7}\cdot COOH$ ... (XIV)

$OH\cdot CH_2\cdot\ (CH_2)_5\cdot\ CH(OH)\cdot CH_2\cdot(CH_2)_7\cdot COOH$ ... (XV)

Fig. 3.2a. Molecular structures of resins

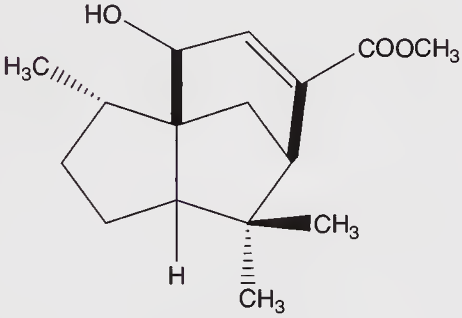




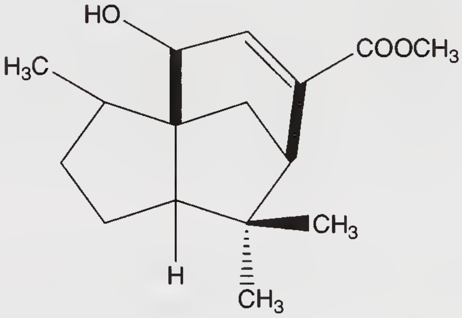
R = CH_2OH, R^1 = COOH ... (XVI)

R = R^1 = CH_2OH ... (XXI)
R = CH_3, R^1 = COOH ... (XXIII)
R = CH_3, R^1 = CH_2OH ... (XXVII)

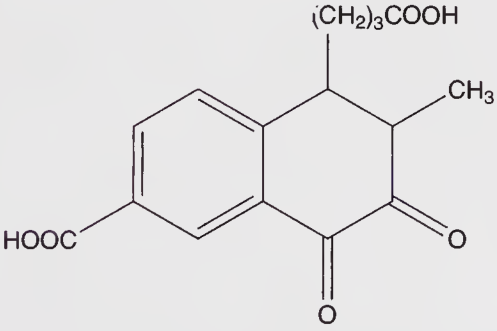
R = CH_2OH, R^1 = COOH ... (XIX)
R = CH_2OH, R^1 = CHO ... (XX)
R = R^1 = CH_2OH ... (XXII)
R = CH_3, R^1 = COOH ... (XXIV)
R = CH_3, R^1 = CHO ... (XXV)
R = CH_3, R^1 = CH_2OH ... (XXVI)



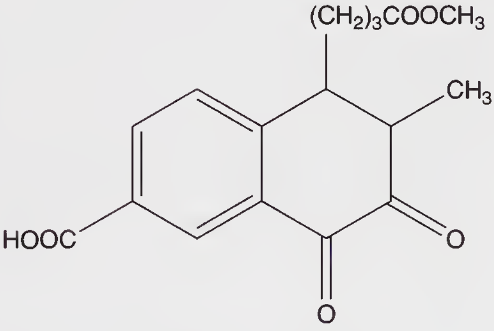
(XXVIII)



(XXIX)



(XVII)



(XVIII)

Fig. 3.2b. Molecular structures of resins

Table 3.1 Yields of various acids obtained by different investigators from shellac, hard resin and soft resin

Acid with M.P. in °C	Percentage present in			
	Shellac[a]	Shellac[b]	Hard Resin[c]	Soft Resin[d]
Myristic			0.30	
Palmitic			0.50	
Stearic	0.73	0.50		1.30
Myristoleic				
Palmitoleic				
Oleic				
6-Ketomyristic, 70-71	0.04	0.25	-	2.50
6-Hydroxymyristic, 58-59 (butolic	7.40	5.00	1.50	9.30
16-Hydroxypalmitic, 92-93	0.80	0.50	-	2.00
16-Hydroxy-cis-9-palmitoleic, 17-19	1.40	1.50	-	1.00
Threo-9,10-Dihydroxymyristic, 78-79	-	3.00	-	13.20
Threo-9,10-Dihydroxymyplalmiticc,93-94	-	1.00	-	-
10,16-Dihydroxypalmitic, 76-77	-	-	-	2.00
9,10,16-trihydroxypalmitic (aleuritic),100-101	21.80	22.00	40.00	14.00
(a) iso-Aleuritic,97-97.5				
(b) iso-Aleuritic,93-94	11.30	-	-	-2.30
	1.40			
(a) Unidentified aliphatic, 83-84				
(b) Unidentified aliphatic	-	-8.00	-	0.25-
Unidentified polyhydroxy compound	-	2.00	-	-
Shellolic, 205-206	10.00	-	-	6.50
Epishellolic, 236-238	1.80	-	-	-
Jalaric, 178-180	-	-	-	-
Laccijalaric, 164-65	26.00	24.00	46.00	36.00
Laksholic,181-83	2.60			4.10
Epilaksholic, 201-203	-	-	-	-
Laccishellolic, 196-198	-	-	-	-
Epilaccishellolic, 235-236	-	-	-	-
Laccilaksholic	-	-	-	-
Balance	14.73	32.25	17.70	5.55

[a]Sengupta, 1970; [b]Christie *et al.*, 1964; [c]Khurana *et al.*, 1964; [d]Agarwal *et al.*, 1976.

as well as from soft resin which he believed to be lactonic in nature. Almost simultaneously Kamath and Potnis (1955) also separated a similar acid from *jalari* (*Shorea talura*) seedlac which they named as Jalaric acid. It is believed to be present to the extent of nearly 1% in the free state (Sengupta, 1953-1955). Pure Jalaric acid (M.P. 178° to 180°C; $[\alpha]_D^{26}+ 36^o$; 2, 4-DNP, M.P. 241° to 242°C) was later obtained by Wadia *et al.* (1969) and has the molecular formula $C_{15}H_{20}O_5$. It contains 1 carbonyl, 1 carboxyl and 2 hydroxyl groups and an α, ß-unsaturated carboxyl. It showed following structural features: (IR: OH 3443, 3433, 1134, 1106, 1068 and 1031 cm^{-1}), CHO (2740, 1704/cm) and α, ß- unsaturated carboxyl (UV: λ_{max} 220 nm; ε 6200; IR: COOH 1684cm^{-1}; C=C 1631cm^{-1}, possibly trisubstituted).

The acid underwent smooth oxidation at room temperature with alkaline Ag_2O to yield shellolic acid (XVI) Fig. 3.2.b (~25%; m.p. 205°-207°C; dimethyl ester, M.P. 150° to 152°C) and another acid (~75%; M.P. 245° to 248°C). Like shellolic acid, this acid was analysed for $C_{15}H_{20}O_6$ and showed spectral characteristics (IR:OH) 3448, 3367, 1135, 1111, 1075 and 1028cm^{-1}), COOH (2667, 1689 and 938cm^{-1}) and α, ß-unsaturated carboxyl (UV: λ_{max} 218 nm, ε 6500; IR: C=O 1678cm^{-1}; C=C 1610cm^{-1}) and hence was considered closely related to shellolic acid. From the PMR spectra of dimethyl shellolate and of the ester of the new acid it was confirmed that the new acid (epishellolic, XIX) is the epimer of shellolic acid. Oxidation of jalaric acid with peracetic acid gave only epi-shellolic acid (XIX) Fig.3.2.b. From these observations and the PMR study absolute configuration of (+)-jalaric acid has been derived (XX) Fig.3.2.b.

Laksholic and epilaksholic acids

During the preparation of shellolic acid in large-scale by the method of Cookson *et al.* (1962), Wadia *et al.*(1969) noticed presence of two more new acids which after isolation were termed laksholic (M.P.181° to 183°C) and epilaksholic (M.P. 201° to 203°C) acids. Both the acids were analysed for $C_{15}H_{22}O_5$ and titrated for monobasic acids. Besides OH groups, the α, ß -unsaturated carboxyl function was also present in their IR spectra which suggested these to belong to shellolic acid group. PMR spectra conclusively proved latter to be the epimer of the former and that the secondary COOH group at C_7 in shellolic (epishellolic) acid has been replaced by CH_2OH and structure was confirmed as (XXI) and (XXII) respectively. Fig.3.2.b.

They subjected Jalaric acid to prolonged alkali exposure (20%, 10 days, room temperature) and isolated shellolic, epishellolic, laksholic and epilaksholic acids from the product in the approximate ratio of 2.2:1.4; 1.2: 1 respectively. This led them to suggest that Jalaric acid may in fact be the primary acid and the others are produced by Cannizzaro and epimerisation type of reaction.

Laccijalaric, laccishellolic, laccilaksholic, epilaccishollolic and epilaccilaksholic acids

Singh *et al.*(1969) isolated two more acids (M.P.196° to 198°C and 235°

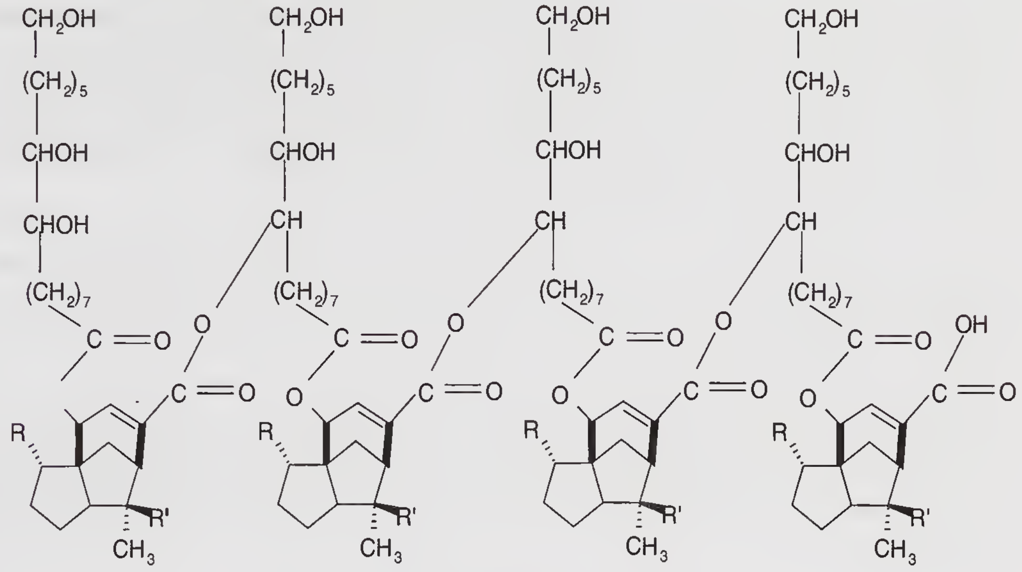
to 236°C) whose dimethyl esters were analysed for $C_{17}H_{24}O_5$ (M.P. 85° to 87°C and 94° to 95°C; $[\alpha]_D$ +44.5 and 52.9). The dimethyl ester of the former showed following structural features: IR : OH (3461, 1110, 1050cm^{-1}) and a tri-substituted olefinic linkage conjugated with a COOMe group (UV: λ_{max} 226 nm, ε 6300). The dimethyl ester of the latter acid showed following structural features: IR: OH (3420, 1110, 1055cm^{-1} COOMe (1710cm^{-1}) and, an olefinic linkage (1640 cm^{-1}) being tri-substituted (815, 775cm^{-1}); UV: λ_{max} 226 nm, ε 5600. Based on the above and PMR data they deduced the structures (XXIII and XXIV) of these two acids, the first acid being the epimer of the second and termed them laccishollolic and epilaccishollolic acid respectively.

Singh *et al.*(1969) also isolated another aldehydic acid corresponding to epilaccishellolic acid. The acid was analysed for $C_{15}H_{20}O_4$ (2,4-DNP, M.P. 235° to 236°C, $[\alpha]_D^{25}$ +26.31°). It showed following structural features: IR: OH (3380, 1040, 1020cm^{-1}), a trisubstituted olefinic linkage conjugated with COOH:IR 1690cm^{-1}) UV: λ_{max} 217 nm; ε 7400 O=C (1630cm^{-1}) and a CHO group. PMR also showed presence of two quarternary methyls. A comparison of its PMR spectrum with that of Jalaric acid revealed identical stereochemistry, the only important difference was replacement of CH_2OH signal in Jalaric acid spectrum by an additional quaternary Me spectrum. Thus, new acid was formulated as (XXV) and named laccijalaric acid.

Alkaline Ag_2O oxidation of laccijalaric acid furnished epilaccishellolic acid (XXIV) and reduction with $NaBH_4$ gave corresponding hydroxy acid, epilaccilaksholic acid (XXVI), $C_{15}H_{22}O_4$, M.P. 206° to 208°C; $[\alpha]_D^{25}$ +35.5°; UV : λ_{max} 218 nm, ε 6270); IR : OH (3220, 3100, 1095, 1060, 1018cm^{-1}), COOH (1710cm^{-1}); C=C (1640, 820cm^{-1}), C-Me_2 (1380, 1365cm^{-1}; methyl ester, M.P. 124° to 125°C.

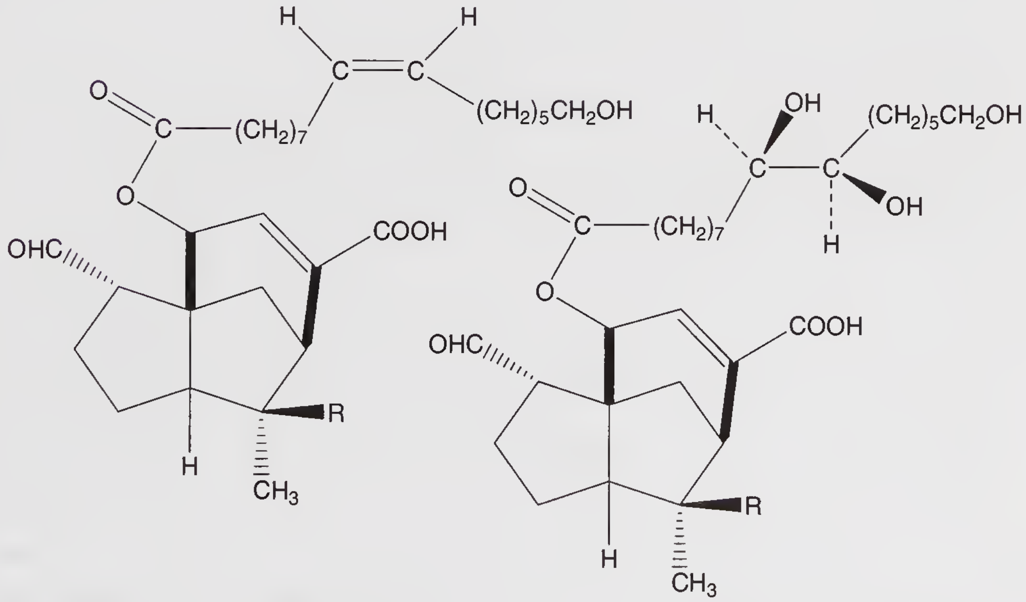
Treatment of laccijalaric acid with alkali (20%, 10 days) at room temperature resulted in formation of laccishellolic and epilaccishellolic acids together with their Cannizzaro alcohol counterparts laccilaksholic (XXVII) and epilaccilaksholic acids. This reaction suggested that laccijalaric acid may be primary product of hydrolysis.

The cedrene skelton for shellolic acid (and related acids) was well established by confirmatory degradative and X-ray studies. The cedrene skelton for laccijalaric acid and related acids has also been well established by Sukh Dev, 1974. Laccijalaric acid by Wolff H shner reduction (Huang. Minlon modification) was converted (after esterification) into two expected epimers (XXVIII and XXIX), Fig.3.2.b. The compound XXIX was next synthesized from a–cedrene through different stages of oxidation, esterification and reduction. These two hydroxy acids derived from laccijalaric acid and a–cedrene were found identical in all respects: M.P.90° to 91°C; $[\alpha]_D^{26}$ +47.2° and +45.5°; λ_{max} 232 nm (ε 6430 and 5730); IR:OH



(XXX)

R = CHO / COOH R′ = CH_2OH/CH_3



R=Me ...... (XXXI)
R= CH_2OH ...... (XXXII)

R=Me ...... (XXXIII)
R= CH_2OH ...... (XXXIV)

Fig. 3.2c. Molecular structures of resins

(3420 cm^{-1}), COOMe (1715cm^{-1}) and C=C (1645, 790, 360cm^{-1}). Since the absolute stereochemistry of (-) α-cedrene is well known, this correlation established the absolute configurations of these new acids. Presence of various terpenic acids, has also been confirmed by other investigators (Sengupta, 1970; Agarwal *et al.*, 1976, and Seshadri *et al.*, 1971) to consider epishellolic acid to be a primary product of hydrolysis.

Yet another new terpenic acid, a liquid, was isolated from one of the fractions of hard resin by Prasad and Sengupta (1975). It showed following structural features: IR:OH (3450 (very weak), 1130, 1080, 1040cm^{-1}), COOH (1730 cm^{-1}), (1740 cm^{-1}) and C=C (1600, 1580, 750cm^{-1}); the olefinic linkage possibly trisubstituted (UV: λ_{max} 210 nm). Thus the acid appeared to be one more aldehydic acid, having a second point of unsaturation. The possibility of presence of its corresponding acids and their Cannizaro alcohol counterparts in the hydrolysate can also be anticipated.

STRUCTURE OF LAC RESIN

However, at present almost all of the constituent acids of lac resin are known but it is not yet fully known how these are linked up to form this versatile resin. Earlier investigators have put forward some arbitrary structures but none satisfy chemical and physical properties of the resin. An attempt was made by Singh *et al.* 1974 to put forward structures of some pure components of the resin. They had isolated a pure fraction (M.W. 2095±110) in an yield of ~12% from hard resin. By means of alkaline silver oxide hydrolysis/oxidation, esterification, formylation and GLC analyses of this, they found that for every one mole of laccijalaric acid approximately 3 moles of jalaric acid and 4 moles of aleuritic acid are generated. Thus they concluded that in pure lac resin there are aleuritic acid and terpenic acids (jalaric/laccijalaric acid and derived dicarboxylic acids) in a ratio of 1:1. Of the 4 terpenic acids, there are 3 jalaric/epishellolic acid and one laccijalaric/epilaccishellolic acid. This molecule should have a molecular weight of 2194, which was in close agreement with the observed value. Based on oxidation, hydolysis and identification of products as well as detailed analysis of the NMR spectra they deduced the possible linkages of the acids. According to them the structure (XXX) Fig. 3.2.c, appears to be most suitable for pure resin fraction, which is fully consistent with the NMR data and meets the major findings from chemical degradation. Molecular structures of resins are illustrated from Fig. 3.2 a-c.

Four essentially pure acid esters were isolated from soft resin fraction following a sequence of degradative and spectroscopic studies (Singh *et al.,* 1974). The ester I series were shown inter-esters derived from one molecule each of laccijalaric acid/jalaric acid and 16-hydroxyhexadec-cis-

9-enoic acid while the ester II series from one molecule each of laccijalaric/jalaric acid and aleuritic acid. On the basis of these evidences, it was concluded that these esters together constitute bulk of soft resin and were designated laccijalaric ester I (XXXI), jalaric ester I (XXXII), laccijalaric ester II (XXXIII) and jalaric ester II (XXXIV) respectively, Fig.3.2.c.

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4

Chemistry of lac dye and lac wax

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LAC DYE

NATURAL DYES appear a more sustainable source of colourants compared to synthetic counterparts, which are derived from non-renewable resources. Natural colourants are used widely in food and beverage industry. Use will probably increase with the need to have colourants that produce the required colour but with minimum risk to consumers. Manufacturers and processors of synthetic dyes are required to address potential health, effluent disposal and other environmental problems.

Two major groups of anthracenes contain several well-known dyes. anthraquinones, *e.g.*, alizarin, mungistin, purpurin from Madder family; cochineal, kermes and lac (all derived from insects). Lac dye is a red-coloured natural dye, which is present in the body fluid of lac insect, *Kerria lacca* (Kerr) as the alkali salt. It is obtained during washing of stick-lac for preparing seedlac. Pure dye is sparingly soluble in water, orange red in acidic medium and reddish violet in alkaline medium. In alkaline solutions, it decomposes rapidly. It gives coloured lakes with inorganic mordant and was formerly employed for dyeing wool. Schmidt (1887) prepared pure dye from commercial cakes, in the form of a brownish-red crystalline powder decomposing without melting at 188°C, and called it 'laccaic acid'. Dimroth and Goldschmidt (1913) suggested $C_{20}H_{14}O_{10}$ as its empirical formula. Mayer and Cook (1943) considered it to be a dicarboxylic acid of hydroxyanthraquinone. Mitrea (1936) was able to separate laccaic acid into two laccains, $C_{18}H_{12}O_9.2H_2O$ (red needles; 80%) and $C_{25}H_{18}O_{12}$ (yellow plates), through fractional crystallization from ethyl acetate. Kamath (1956) reported that lac dye from Jalari lac contains 1.5 to 1.6 % of combined nitrogen and was able to separate it into two components: one containing nitrogen and other free from nitrogen.

Laccaic acid (Fig. 4.1.a) prepared by Dimroth and Goldschmidt contained about 2 % nitrogen, apparently present as the primary amino

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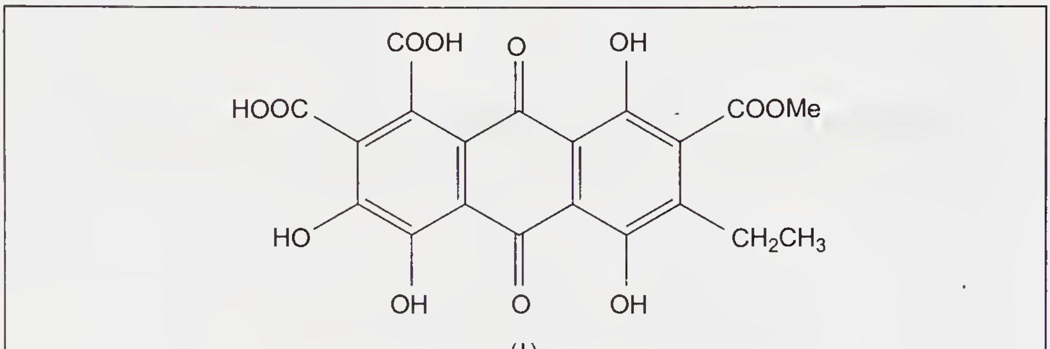


(I)

4.1a. Structure of laccaic acid

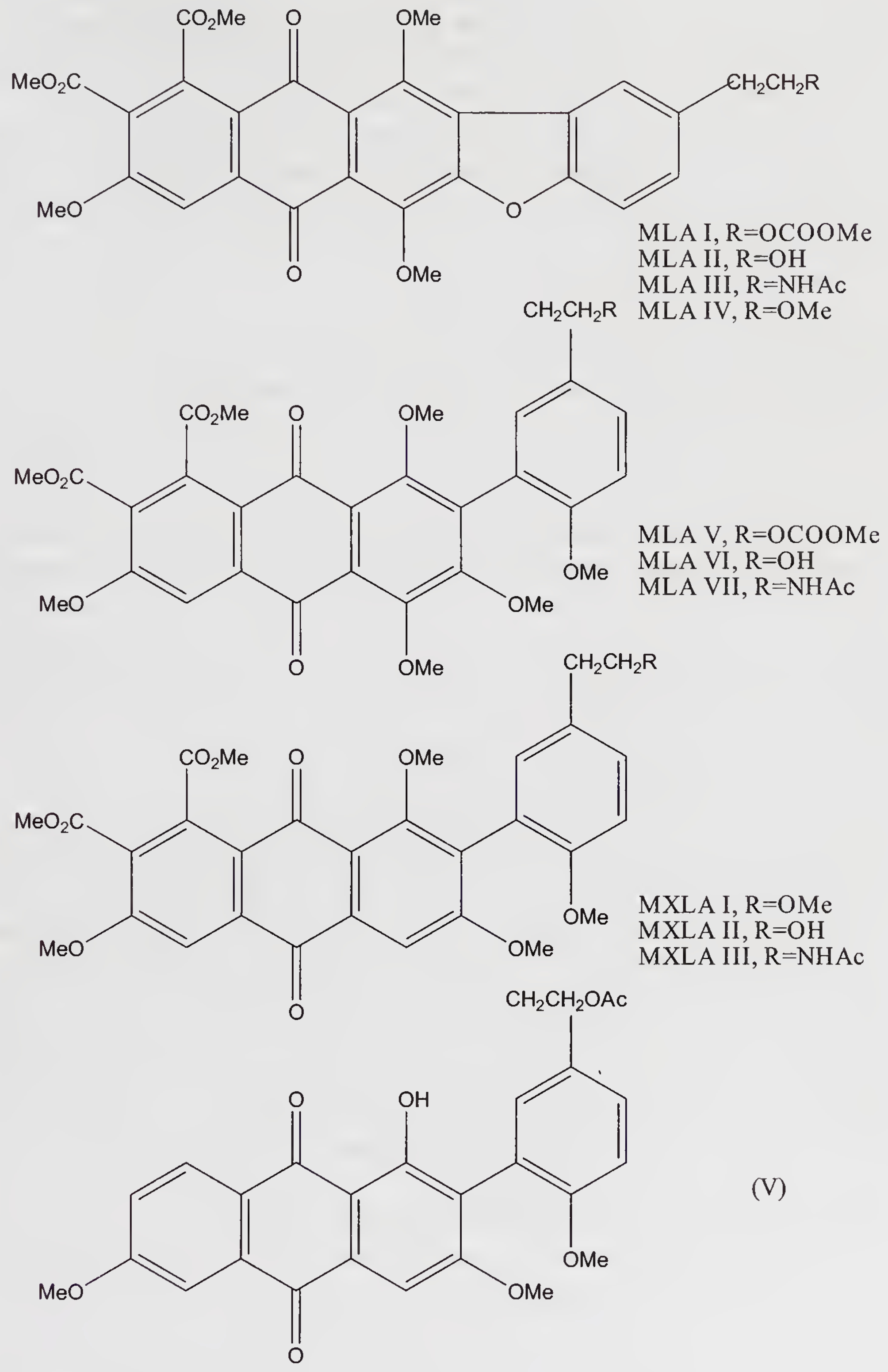
group (van Slyke estimation), Venkataraman and Rama Rao, 1972. Colour reaction showed that laccaic acid is a purpurin derivative, and there was no evidence for presence of a C-acetyl or a C-ethyl group as in (I). The following method was then used for isolation of lac pigment in standard form (Venkataraman and Rama Rao, 1972). Stick-lac was extracted with water at room temperature and passed through a column of cation-exchange resin (H form) from cashew-nut shell liquid and concentration under reduced pressure in a flash evaporator at a temperature not exceeding 45° gave a crystalline dye, which was found (by paper chromatography) to consist of two components with Rf values 0.09 and 0.45; the latter being major fraction (Venkataraman and Rama Rao, 1972). The major component was separated by passing through CNSL resin or Dowex-SO. It crystallized readily from water, but repeated crystallization gave a pigment containing 0.5 to 1.4% nitrogen. Countercurrent distribution between aqueous acetic acid and isopropyl acetate, as well as chromatography on diethylaminoethyl cellulose, indicated presence of at least four constituents (Venkataraman and Rama Rao, 1972).

Prolonged methylation of laccaic acid with dimethyl sulphate and potassium carbonate in boiling acetone gave a variety of golden yellow crystalline ethercesters, of which 6 have so far been separated as homogeneous compounds by TLC on silica gel (multiple development with varying proportions of benzene and acetone) Pandhare *et al.,* 1966. The six methylated laccaic acids (designated MLA I, II, III, V, VI and VII, Fig. 4.1.b) have melting points 194°, 227°, 243°, 115°, 189° and 116°C. Structures of the laccaic acids have been suggested on the basis of mass spectral and NMR data (Venkataraman and Rama Rao, 1972). Of the six MLAs, two were found to contain nitrogen.

Preparation of water soluble lac dye

Technical grade

Stick-lac wash-water is acidified with sulphuric acid/hydrochloric acid



MLA I, R=OCOOMe
MLA II, R=OH
MLA III, R=NHAc
MLA IV, R=OMe

MLA V, R=OCOOMe
MLA VI, R=OH
MLA VII, R=NHAc

MXLA I, R=OMe
MXLA II, R=OH
MXLA III, R=NHAc

(V)

Fig. 4.1b. Structure of Methylated laccid acid (MLA)

(0.1% on the vol. of water) and the precipitate is allowed to settle in tanks. The supernatant clear liquor is collected by filtration. The acid precipitated sludge is separately extracted thrice with boiling water for removal of dye and washings were mixed with previous collections.

The mixed filtrate is then treated with calcium carbonate ($CaCO_3$) or quicklime till the liquor becomes almost colourless. The calcium salt of dye, which separates out is collected by filtration, washed with water. The cold suspension of calcium salt of lac-dye in water is acidified with 10% aqueous acid solution and kept for 7-10 days at room temperature when the dye crystallizes out (Ghosh *et al.*, 1964, and Ghosh and Sengupta, 1977). It is filtered, washed and dried (yield approx.0.5% on the weight of stick-lac, dye content 80 to 90% depending on the quality and age of stick-lac).

Pure (food) grade

Method A: The calcium salt of dye is triturated with requisite quantity of sodium carbonate solution which precipitates calcium as calcium carbonate and the dye goes in to solution as sodium salt. The filtrate obtained is passed through a column of cation exchange resin. Concentration of the filtrate, preferably under reduced pressure, pure dye, bright red crystals, separates out on keeping concentrate for 3 to 4 days. The dye obtained is pure and soluble in water (Prasad, 2005).

Method B: Technical grade dye is further purified by dissolving it in mild alkali, filtering the insolubles, acidifying the filtrate and finally keeping it for 8 days for crystallization. The crystallized dye is filtered, washed and dried (yield approx.0.25% on the weight of stick-lac, Purity 99% and above). The purified lac dye is bright red. It is sparingly soluble in cold water (0.13 to 0.14%) but completely soluble in dimethyl formamide. It can be used for colouring food materials as it gives deep orange-red in aqueous solution like colour of beverages and cold drinks available in the market (Pandhare *et al.*, 1969). The method B is better than A as it avoids evaporation of large volume of water at room temperature and the method is easier as regard to filtration at different stages.

Separation of laccaic acids (water-soluble lac-dye)

The pioneering study on the establishment of structure of laccaic acids was done by Venkataraman and Rama Rao (1972).

Laccaic acid A

When crude laccaic acid is dissolved in n-butanol saturated with 0.3 N HCl, the mixture is filtered and the clear bright red solution in organic phase is chromatographed on a column of polycaprolactam powder, using same solvent system for development and elution. Minor fast- moving fraction is obtained from two main fractions. Extraction of each with saturated aqueous sodium acetate and acidification with ice-cold conc.,HCl hydrochloric acid, yield laccaic acid A and B respectively. Laccaic acid A separates as bright red needles and can be recrystallised from water or methanol. Laccaic acid A yield MLA III and MXLA III by appropriate reactions. Identity was established from mixed M.P. and superimposable IR spectra. The structure proposed for laccaic acid A was confirmed by Burwood *et al.* (1967).

Laccaic acid B

Laccaic acid B is obtained as a pure homogeneous compound after separation from a minor fraction (laccaic acid C), which is the alcohol corresponding to laccaic acid A, and that the carbonate group in MLA V is formed by the action of dimethyl sulphate and potassium carbonate *via* dimethyl carbonate (Pandhare *et al.,* 1967). The conversion of laccaic acids A and B to common derivatives was achieved. Venkataraman and Rama Rao (1972) discussed it in detail. Laccaic acid A and B constitute 90% of the total dye.

Laccaic acid C

Chromatography of laccaic acid on a column of cellulose powder (solvent system BAW, 6: 1: 2) results in the appearance of the major components A and B as a single band; the minor fraction (Rf 0.09 on paper) separates into two bands from which laccaic acid C and E are isolated, the latter in very small amount. The two new laccaic acids together constitute about 5 % of the total dye. Laccaic acid C is crystallised from methanol in dark red needles *(dec.* above 360^0; N content 2.8%). The structure of laccaic acid C was suggested from chemical and spectroscopic analysis. It is the first naturally occurring anthraquinone carrying an amino acid side chain, and its biosynthesis (Fig. 4.1 e and f) involves oxidative coupling of a purpurin derivative with tyrosine (Venkataraman and Rama Rao, 1972).

Laccaic acid E has been suggested deacetyl laccaic acid A; it has not yet been entirely isolated free from laccaic acid C, but acetylation of laccaic acid E and hydrolysis of the O-acetyl groups gave a product chromatographically identical with laccaic acid A.

Laccaic acid D

An acetone solution of crude laccaic acid, isolated as described earlier from *rangeeni* stick-lac (host trees *Butea monosperma* and *Zizyphus mauritiana),* is passed through a short column of silica gel and a fast moving yellow band is eluted with the same solvent. Removal of the solvent and crystallisation from water yield yellow needles *(dee.* above 300°) of laccaic acid D, it is sharply distinguished from other laccaic acids, which are derivatives of 2-phenylanthraquinone. Laccaic acid D is identical with xanthokermesic acid, and on decarboxylation by reftuxing with diethylaniline it yields desoxyerythrolaccin. (Mehandale *et al.,* 1968).

The colouring matter of lac larvae

Singh *et al.* (1966) suggested that colouring matter of lac larvae, "lacciferic acid", belongs to ommochrome group of pigments (Butenandt and Schafer, 1962) and resembles ommins in complexity and in spectral properties. They opined that "laccaic acid seems to be a degradation product and belongs to the same group". Their conclusions were mainly based on the chromatographic behaviour of the products obtained by acid and alkaline hydrolysis of 'lacciferic acid' and were different from those of Venkataraman and Rama Rao, 1972. Chromatography of a solution of' lacciferic acid in phosphate buffer (pH 6.8) on Bio-gel P_2 conclusively showed that it mainly consisted of laccaic acids A, B and C; besides these low molecular weight components, it contained a coloured fraction identified as laccaic acid C associated with a protein (Shaikh, 1969).

The colouring matters of seed lac (water insoluble lac-dye)

A water-insoluble yellow pigment, erythrolaccin, was isolated by Tschirch and Ludy (1923) and the structure Fig. 4.1c was suggested, which

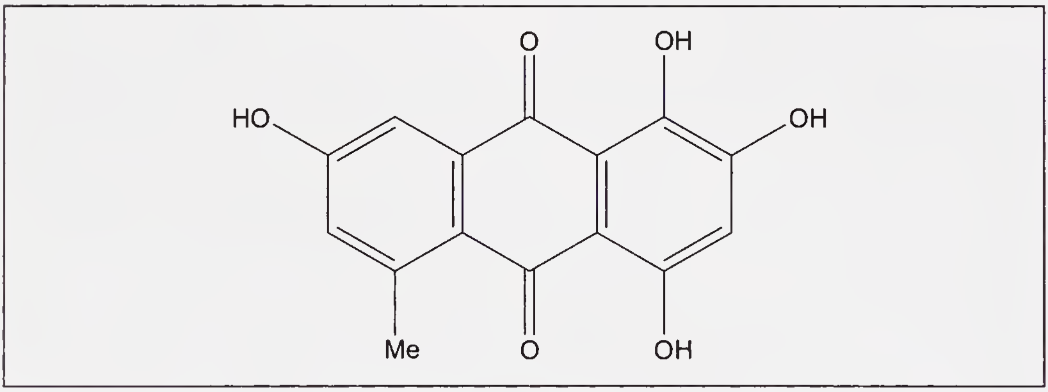


Fig. 4.1c Erythrolaccin

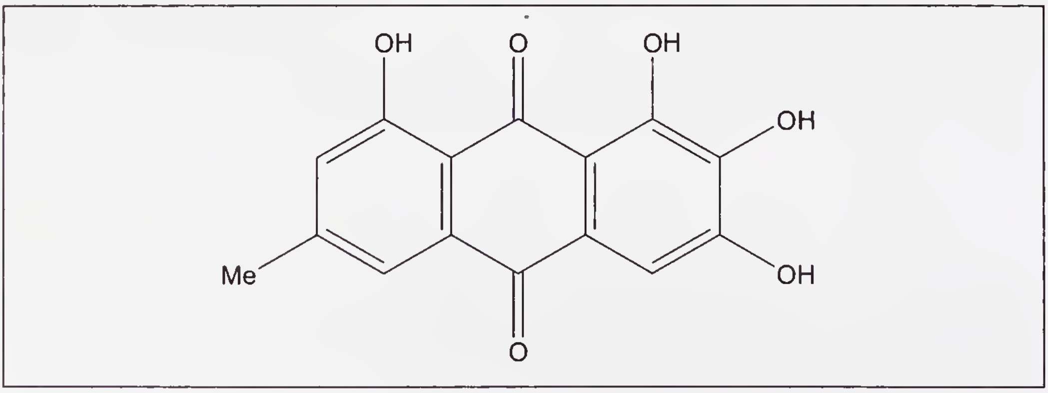


Fig. 4.1d A pigment isolated from *Eriococus confusus*

was modified by Venkataraman and Rama Rao (1972). On the basis of NMR spectral data (Bhide *et al.,* 1965). Yates *et al.* (1964) arrived at the same conclusion independently, but their synthesis by the condensation of 3,5-dimethoxyphthalic anhydride with 4-methyl-catechol was not free from ambiguity. Confirmation of the revised structure was obtained by the synthesis involving a series of reactions starting from 3-chlorophthalic anhydride and 4-methyl catechol 2-methyl ether (Bhide and Rama Rao, 1969).

Two new pigments, desoxyerythrolaccin and isoerythrolaccin, were isolated from seedlac and their structures were suggested (Venkataraman and Rama Rao, 1972, and Mehandale *et al.,* 1968,1972). After removal of erythrolaccin and chromatography of the residue on polyamide, using ethanol and formic acid-water (8.5: 0.5: 1. 0), the fast moving band gave desoxyerythrolaccin (0.02%), followed by isoerythrolaccin (0.003%) and erythrolaccin. The structures of desoxyerythrolaccin and isoerythrolaccin,

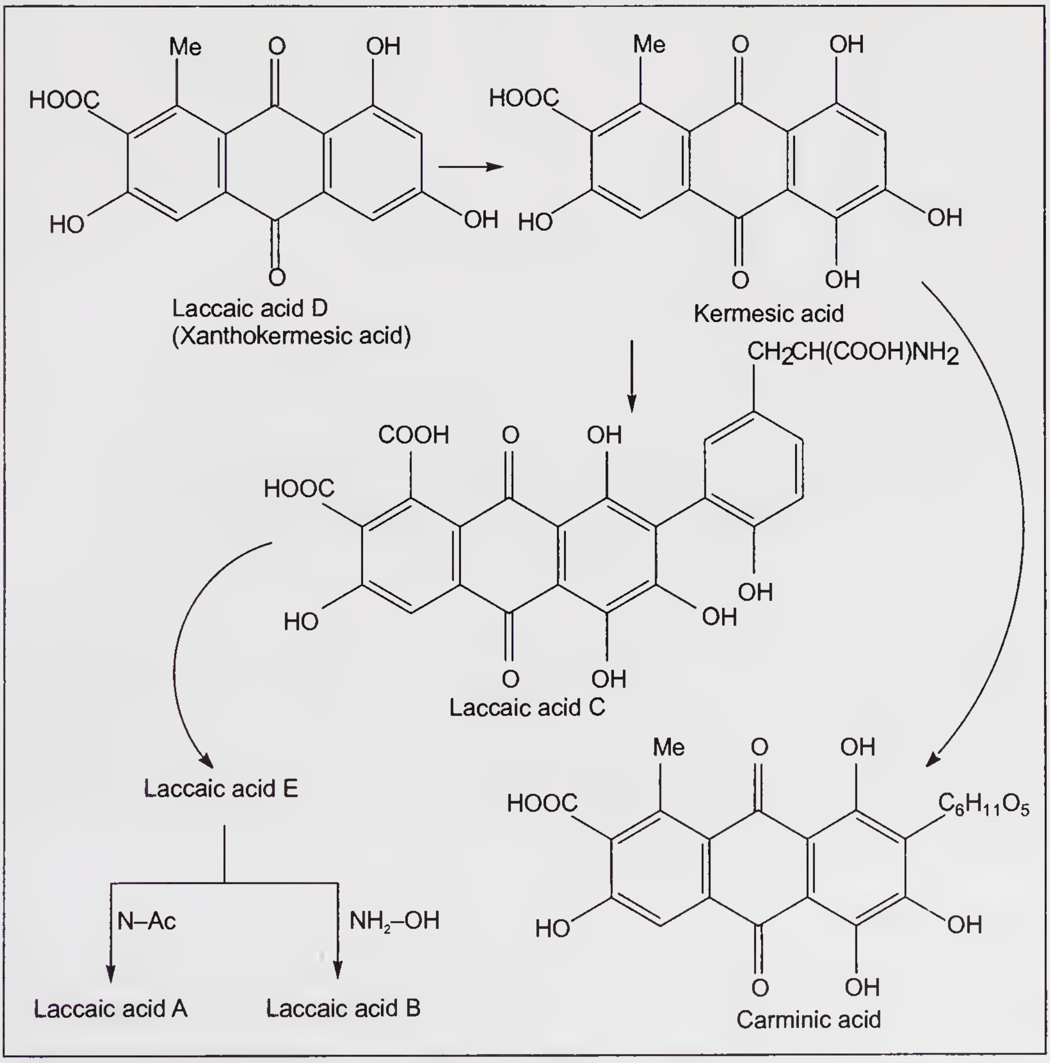


Fig 4.1e. Biosynthesis of some pigments from anthraquinone (Venkataraman and Rama Rao, 1972)

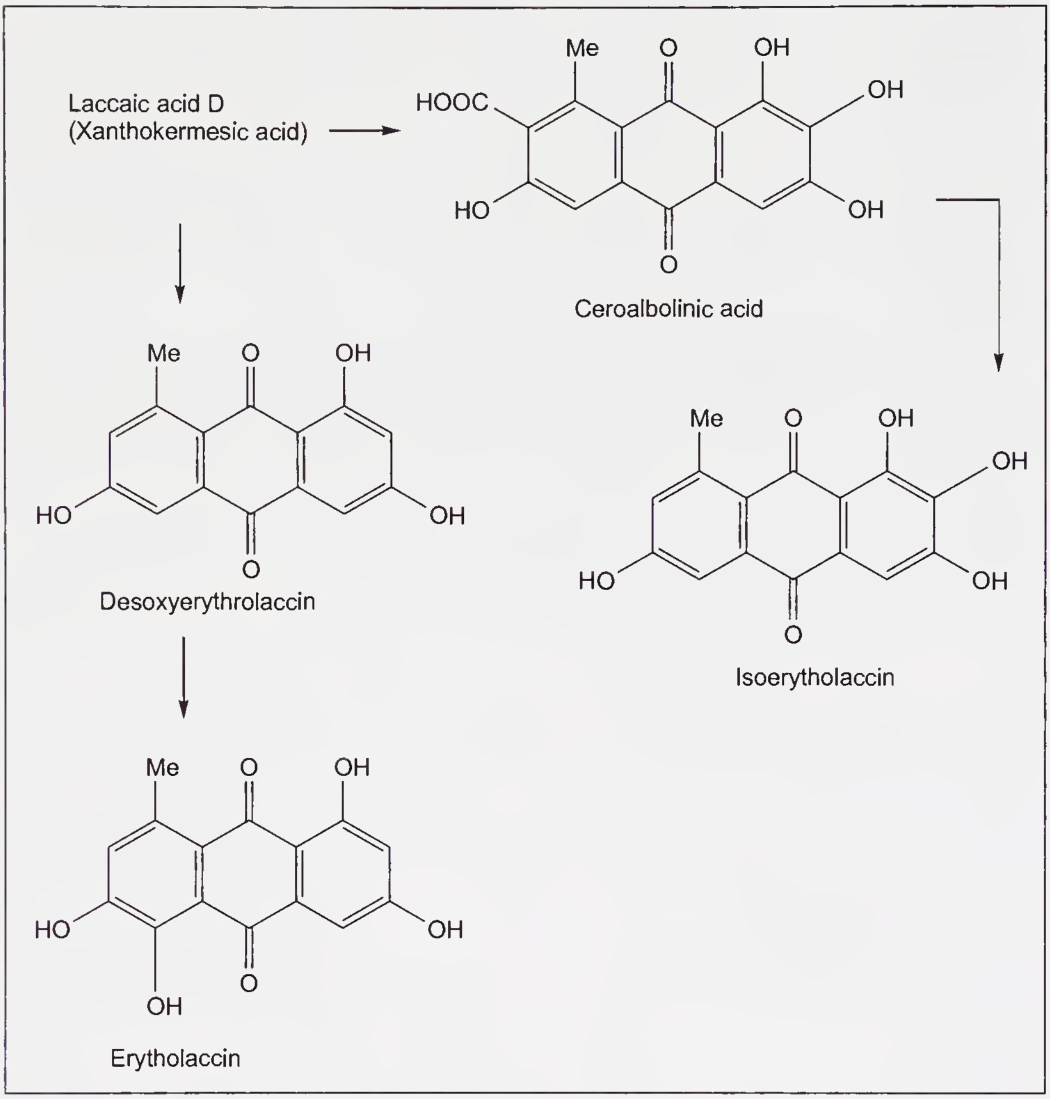


Fig. 4.1f. Biosynthesis of some insect pigments from anthraquinone (contd.) (Courtsey: Venkataraman and Rama Rao 1972).

Fig.4.1.f, were confirmed by synthesis. Condensation of 3,4,5-trimethoxyphthalic anhydride with m-cresol methyl ether in an aluminium chloride-sodium chloride melt at 180°C gave 2 products: one was identical with isoerythrolaccin, characterized as its tetramethyl ether, and the other was Fig. 4.1d, a pigment isolated from the insect, *Eriococcus confusus,* Maskel by Chan and Crow (1966).

Biosynthesis

Venkataraman and Rama Rao (1972) suggested a scheme for biosynthesis of quinone (Figs. 4.1e and f). Xanthokermesic acid (laccaic acid D) is believed to play the main role in the biosynthesis of kermesic acid, carminic acid, laccaic acids A, B, C and E, desoxyerythrolaccin, erythrolaccin and isoerythrolaccin.

Distinguishing between certain isomeric anthraquinone derivatives

Biosynthetic scheme suggested in Figs.4.1e and f threw light on the orientation of hydroxyl and carboxyl groups in anthraquinone ring in laccaic acids A, B and C, in kermesic and carminic acids. The structure of desoxyerythrolaccin was confirmed by synthesis from which the structures of laccaic acid D and kermesic acid followed. Mehandale *et al.* (1972) developed a general method for distinguishing between pairs of isomers *viz.*, (a) kermesic and isokermesic acids, and (b) laccaic acid A and the isomer Fig. 4.1g.

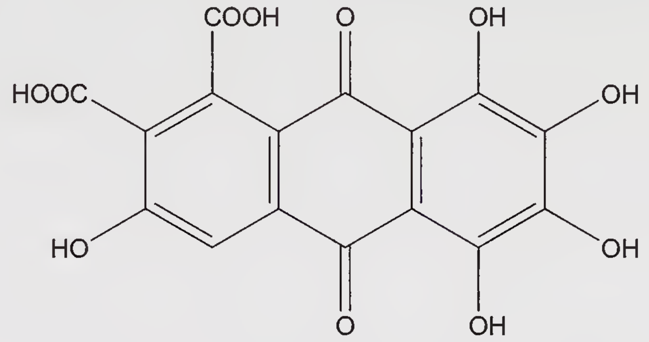


Fig. 4.1g Laccaic acid A and its isomer

The structure suggested for desoxyerythro-laccin was confirmed by diamagnetic shift of the 4, 5~protons in the NMR spectrum of the corresponding anthrone in DMSO (Venkataraman and Rama Rao, 1972). The orientation of the substituents in kermesic acid follows because kermesic acid was converted earlier to desoxyerythrolaccin trimethyl ether. Similarly, the orientation of the substituents in rings A and B of laccaic acids A and B was shown by preparing the anthrone (Fig. 4.2), in whose NMR spectrum the two a-protons shifted by more than 0.6 ppm upfield compared with the corresponding anthraquinone (Venkataraman and Rama Rao, 1972).

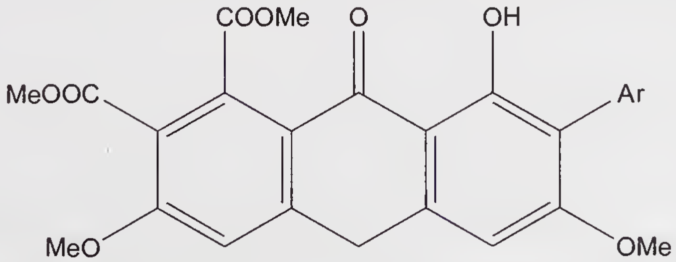


Fig. 4.2 Anthrone

Melting profiles of lac dye by differential scanning calorimeter

Prasad (2005) isolated lac-dye from wash-water of lac factory effluents, through preparation of calcium salt and treatment with acid. Crystallized dye exhibited three melting peaks around 99.3°, 195.1° and 274.5°C (Fig. 4.3). The peaks, in general, were not sharp, multiple crystallization although resulted in some degree of sharpness, yet presence of multiple peaks indicate presence of different fractions of lac dye, presence of which was indicated by Venkataraman *et al.* (1972). Srivastava *et al.* (unpublished work) attempted to crystallize lac-dye from simple water extract of stick-lac, without addition of any additive (unlike Prasad *et al.*). Melting profile of the dye obtained after multiple crystallization by DSC revealed interesting information. The spectrum revealed only one melting peak around 112.4°C (Fig. 4.4), which was sharper than any of the peaks obtained for laccaic acid isolated by Prasad *et al.,* 1982. The single peak indicates

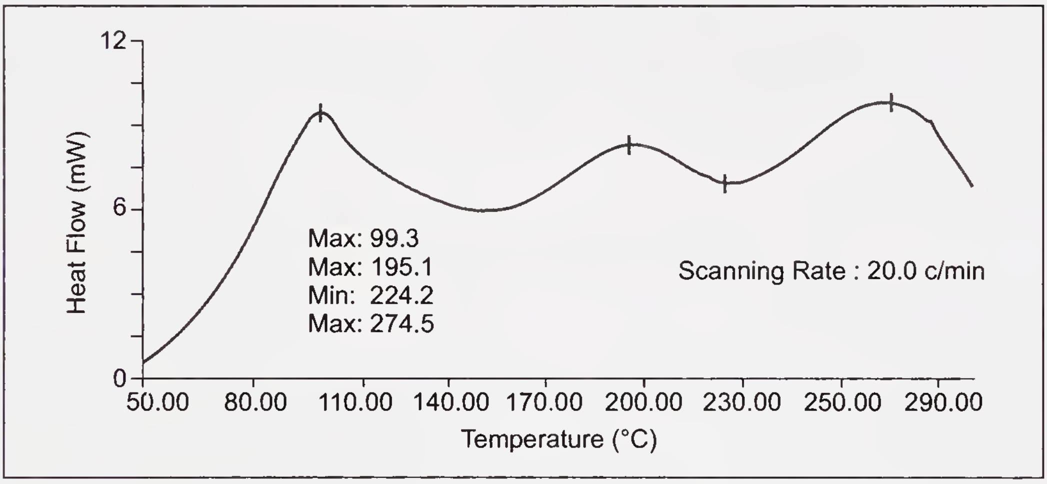


Fig. 4.3 Melting profile of lac dye extracted from effluents of lac factory (Prasad *et al.,*1982)

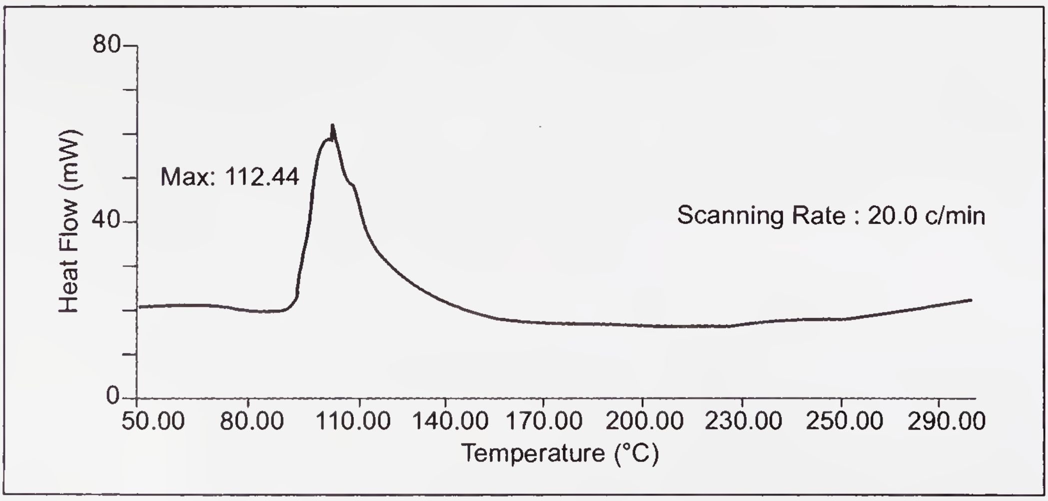


Fig. 4.4 Melting profile of lac dye crystallized from water extract of stick-lac

more homogeneity, absence of different fractions (unlike that obtained by Prasad *et al.,* 1982).

LAC WAX

Lac wax is a constituent of natural resin lac. It is secreted by the lac insect along with the resin, in the form of thin white filaments. It is generally found to the extent of nearly 4-5% in seedlac, 3-5% in shellac and slightly higher percentage in stick-lac (5-6%) (Bose *et al.* 1963).

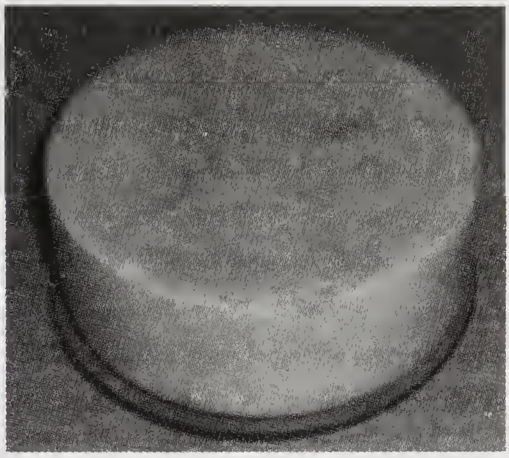


Fig. 4.5.Lac wax

Lac wax (Fig.4.5) is recovered directly during processing of stick-lac and also during the preparation of solvent-based dewaxed shellac generally called shellac wax. Physical and chemical constants of lac wax are discussed in Table 4.1.

The acid value of lac wax was determined from authentic sample at the Institute's laboratory and was found to be 4.8, which is lower than

Table 4.1. Physical and chemical constants of lac wax

Softening point (°C)	Melting point (°C)	Specific gravity	Acid value	Saponi-fication value	Ester no.	Iodine value	Ash content (%)	Author
	58-59		22.1-24.3	79.2-83.0	57.1-60.7	8.8 (Hubl after 18 hrs. action)		Singh (1911)
		1.028						Oslen
							(1932)	
	72-75	0.971-0.980	12-16	20-126				The Netherland Firm of
							Was de	
					Wit N.			
			V.					
	81-82	0.930	12.1	63.8		6.0		F.H.Paul & stern
							Brothers	
	72-82	0.971-0.982 0.972	12.0-24.3	79.126	45.5-104	6.0-8.8	0.08	Chemical literature
72-75	79-80							Bhowmik
							(1944-45)	
						12.2 (Wijs)		Wright
							(1949)	

Table 4.2. Characteristics of lac-wax obtained from stick-lac of different lac host plants (Prasad *et al.* 1984).

Hosts	Wax Cont. (%)	Free Acid cont. (%)	Melting Points (°C)	Acid Value	Iodine value	Saponification value	Ash content (%)	Volatile matter at 150°C (%)	Resin cont. (%)	Penetration value
Palas	6.3	10.2	74-78.5	4.5	4.7	66.2	0.08	1.0	2.6	4
Ber	7.0	12.5	76-82	7.0	8.4	94.0	0.08	1.0	3.0	6
Kusum	6.0	9.0	75-82	3.1	4.0	68.5	0.07	0.9	2.3	6
Arhar	3.0	5.0	74-79	2.5	3.2	65.1	0.07	1.0	2.8	5
Moghania	4.5	9.8	75-79	4.3	6.5	43.1	0.08	0.8	2.8	5

those obtained by the authors in Table 4.1. Lac wax obtained from stick-lac of various lac host plants such as *palas (Butea monosperma), ber (Zizyphus mauritiana), kusum (Schleichera oleosa), arhar (Cajanus cajan)* and *moghania (Flemingia macrophylla)*, was also characterized in Table 4.2 (Prasad *et al.,* 1984).

No significant variation has been noticed in melting point of waxes obtained from various host plants. The wax from *palas* appears to be harder than that obtained from *ber* and *kusum*. Wax content in stick-lac was found least in seedlac obtained from *arhar* and maximum from *ber*. Shellac wax deteriorates slightly as it ages, as evident from the reduced melting point and hardening of the wax (Table 4.3). Dielectric strength of shellac wax has been reported 14 to 17 kV/mm, which is lower than shellac (40 kV/mm).

Table 4.3. Physical constants of fresh sample and after ageing

Physical constants	Fresh sample	After years of ageing
Melting point (drip)	83.7°C	82°C
Softening point	74.5°C	74.5°C
Ball and mill (M.P.)	80.7°C	79.8°C
Fisher-Johns (M.P.)	59°C (min.) and 84.5°C (max.)	65°C (min.) and 82°C (max.)
Penetrometer reading (100 g/5 sec/25°C)	6.5	4.25

Chemical properties and constitution

Kauffman (1837) isolated lac-wax by dissolving shellac in hot-soda solution and skimming off floated wax from surface as a molten mass, having M.P. 78° to 79°C. It was fractionated into two parts - one soluble and another insoluble in alcohol. Two alcohols, $C_{28}H_{58}O$ and $C_{30}H_{62}O$, melissic acid ($C_{30}H_{60}O_2$), M.P. 90° to 90.5°C and a brown substance of the formula $C_{28}H_{54}O_2$, M.P. 80° to 84°C were detected. A dichloride $C_{28}H_{54}Cl_2$ or $C_{28}H_{52}Cl_2$ and a hydrocarbon, M.P. 61° to 62°C, by reduction with HI and P were prepared. Benedikt and Ulzer (1888) isolated palmitic, stearic and oleic acids together with ceryl and myricyl alcohols by treating wax with alcoholic KOH. They noticed that wax contains 50% of free alcohols.

According to Gascard (1893 and 1914), acids, which are combined with approxicately half of the total myricyl alcohol, are melissic, cerotic, oleic and palmitic. Gascard examined residual wax of stick-lac, after the resin was extracted with alcohol, and an ester, lacceryl lacceroate (M.P. 94°C), was isolated. Upon hydrolysis, ester gave laccerol (lecceryl alcohol, $C_{32}H_{65}OH$), which crystallizes in rhomboidal plates (M.P. 88°C) and lacceroic acid ($C_{31}H_{63}COOH$) in rhomboids (M.P. 95° to 96°C).

Tschirch and Schaffer (1926) observed that about 85% of the wax is soluble in boiling alcohol and wax melts at 80° to 81°C. An alcohol, M.P.79°C and acid, M.P.78°C, were separated from the wax. Based on the investigations of Tschirch and Schaffer (1926), following were the conclusions:

- About 85% of lac-wax fraction is soluble in boiling alcohol and consists of an alcohol $C_{25}H_{51}OH$ and an acid $C_{26}H_{52}O_2$
- A boiling alcohol insoluble fraction, consisting about 15%, is an ester of alcohol $C_{32}H_{66}O$ and acid $C_{32}H_{64}O_2$
- About 2% of wax is reported to be a hydrocarbon $C_{25}H_{52}$.

Wright (1949) confirmed findings of Tschirch and Schaffer. It was found that yields of pure products were small in most cases, indicating that there was a large portion of the material left uninvestigated. Warth (1956) suggested composition in Table 4.4.

Table 4.4. Composition of resin-free shellac wax

Esters of wax acids Ceryl lignocerate (M.P. 79°C) Ceryl cerotate (M.P. 84°C) Lacceryl lacceroate (10 to 12%) Ceryl aleuritate (1% or less)	80 to 82%
Free wax acids Lacceroic acid (M.P. 95 to 96°C) Cerotic acid	10 to14%
Free wax alcohols Neoceryl alcohol (tachardiacerol, M.P.80.1°C, Tschirch)Lacceryl alcohol	Less than 1%
Hydrocarbons Pentacosane (tachardiacerin) 2% Heptacosane	2-6%
Lac resins	2-4%

Further, composition of lac-wax was recorded: Acid component 3.1%; alcoholic component 26.4%; Anhydrohydroxy acid1.6%; Esters 66.8% and Hydrocarbons 2.1%. Of which, acids are cerotic, myristic and palmitic acids. Alcoholic components are mixtures of n- primary alcohols, 26 to 34 carbon atoms (C_{26} alcohol, 0.5%; C_{28} alcohol, 4.9%; C_{30} alcohol, 14.9%; C_{32} alcohol, 4.1% and C_{34} alcohol- 2.0%).

The esters are derivatives of C_{26} to C_{32} alcohols and C_{14}, C_{16} and C_{26} to

C_{34} acids. Acids appear to be a mixture of at least 15 different esters with a mean molecular weight of 718.5 and molecular formula of $C_{49}H_{98}O_2$. The hydrocarbon is likely to be a C_{27}, n- aliphatic hydrocarbon. The most important observation is the presence of myristic esters. Myristic acid itself has been fully identified and characterized as its anilide.

Melting of wax extracted from seedlac obtained from different lac producing countries: Srivastava *et al.* (2006) investigated melting profiles of wax extracted from seedlac of various countries by n-hexane using a soxhlet. These were dried and melting profiles were studied employing a (Perkin Elmer) Differential Scanning Calorimeter (DSC 7). Thai seedlac exhibited melting peaks at 57.93°, 72.27° and a small peak at 82.9°C. Dewaxed Thai seedlac gave a melting peak at 57.7°C and a small peak at 82.8°C, indicating the peak at 72.27°C was due to wax present in seedlac. Similarly, Chinese seedlac showed three melting peaks at 58.1°, 70.8° and 82.97°C; dewaxed seedlac showed only one peak at 57°C, revealing that peaks at 70.8 and 82.97°C were due to wax present in seedlac. Indian seedlac exhibited melting peaks at 58.33° and 72.1°C and Indian shellac showed a prominent peak at 65.7°C (resin) and a small peak at 74.89°C (wax). Melting profiles of waxes extracted from Indian, Thai and Chinese seedlacs revealed multiple peaks (Table 4.5).

Table 4.5. Positions of melting peaks (°C) for waxes of different origins

Wax extracted from	Indian seedlac	Thai seedlac	Chinese seedlac
Peaks at (°C)	48.8, 57.7, and 72.1	49.6, 71.8, 97.6, 115.2	72.23 and a small at 49.8

Superimposition of melting profiles of waxes obtained from three origins (Figs.4.6 and 4.7) revealed that there were at least two fractions common to all, possessing melting peaks around 49° to 50°, and 72°C. It appears

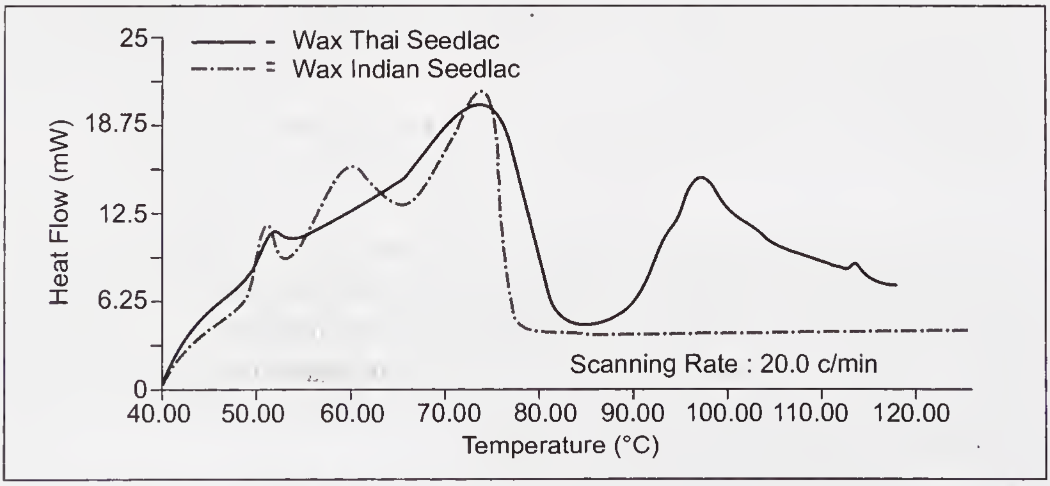


Fig. 4.6. Melting profiles of waxes extracted from Thai and Indian seedlac

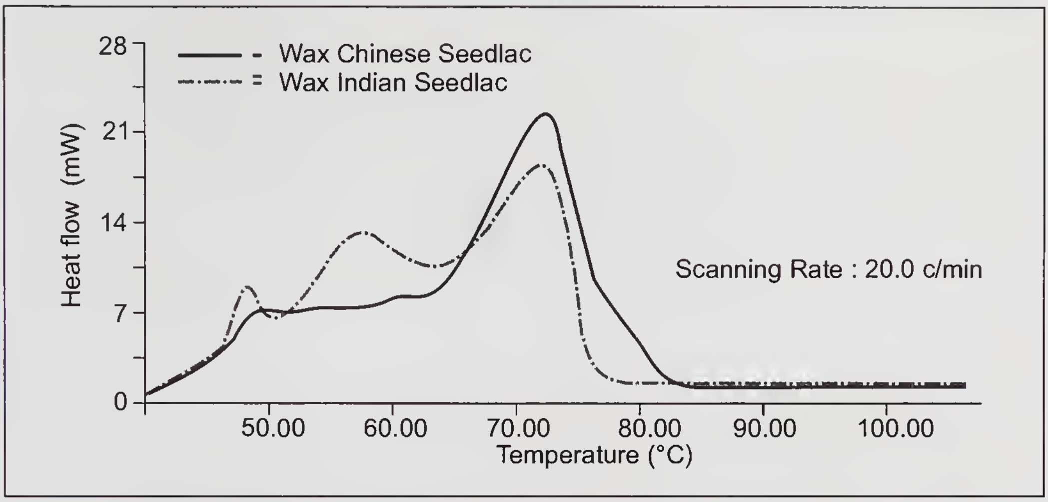


Fig. 4.7 Melting profiles of waxes extracted from Chinese and Indian seedlac

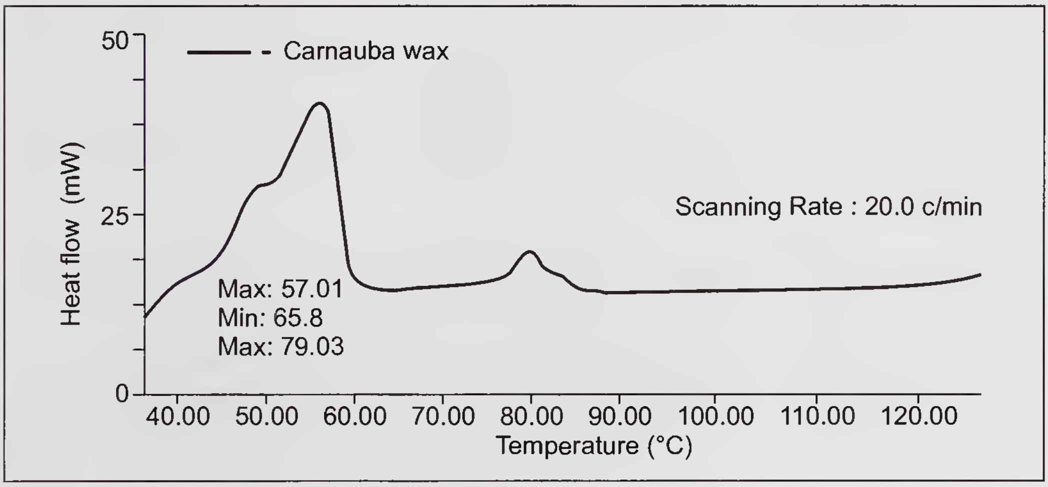


Fig. 4.8 Melting profile of carnauba wax by DSC.

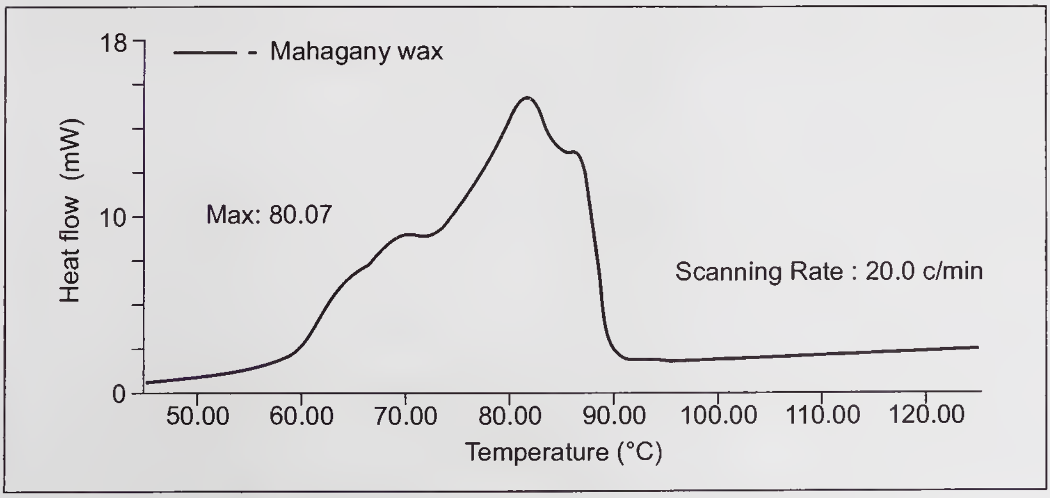


Fig. 4.9 Melting profile of mahogany wax by DSC

that lac insects irrespective of species and hosts (and country) secrete two similar wax fractions. Comparatively high melting wax fractions secreted by Thai lac insects might be due to environmental need for protection of their lives. Waxes of natural origin, carnauba wax (Fig.4.8), mahogany wax (Fig.4.9) and bee's wax (Fig.4.10) all exhibit multiple peaks when examined by differential scanning calorimeter.

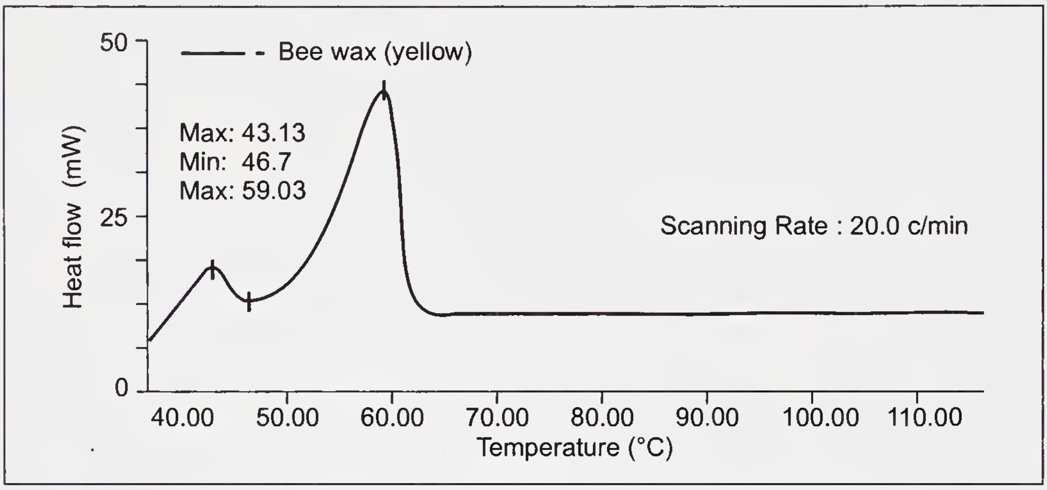


Fig. 4.10 Melting profile of bee's wax by DSC.

Melting profiles of wax extracted from effluents of lac factories, however, revealed peaks at 51.37°, 61.63°, 70,27° and 77.77°C (Fig.4.11). Wax extracted from seedlac is almost in natural form (Figs.4.6 and 4.7); representing true characteristics of lac-wax. Lac-wax from wash water obtained after series of chemical treatments is expected to undergo degradation, yielding more number of peaks at different positions (due to degradation).

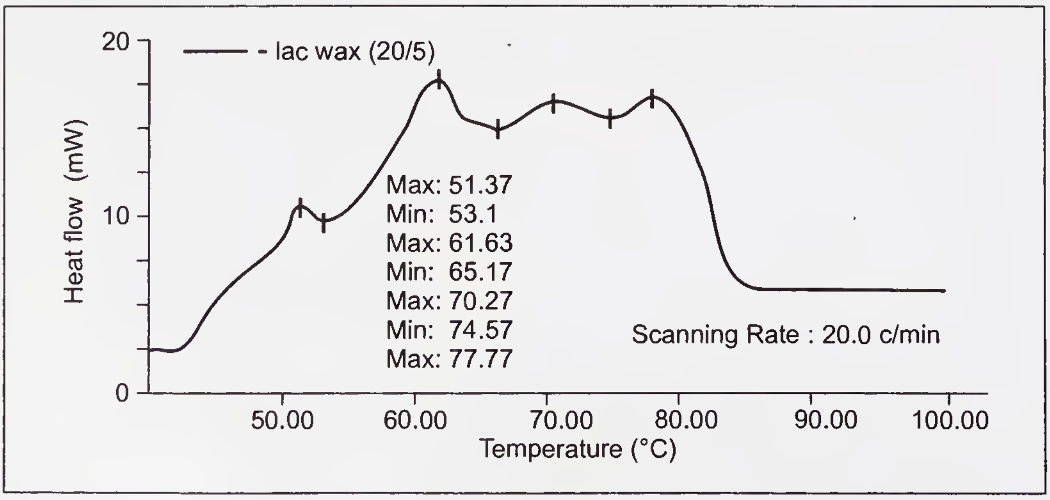


Fig. 4.11 Melting profile of shellac wax from effluents of lac factory

Uses of shellac wax

Principal use of shellac wax has been reported in electrical industry, though it is of general use in formulations where use of a natural wax of a hard type is advantageous. True shellac wax commands high price, and the demand for refined product exceeds supply. High melting point of shellac wax and its high electrical insulation value favour its use as electrical potting compounds and appliances. In shoe creams, addition of a little shellac wax to an otherwise ordinary formula containing montan and paraffin waxes is a means of producing a high lustre. Shellac wax sold for polishes is said to be frequently admixture with Chinese insect wax, tallow, resin and montan wax. It also has application in floor and car polishes, food, confectionery and tablet finishing, lipsticks, crayons and tailor's chalk. Noncle (1939) formulated an emulsifiable wax stock consisting of candelilla wax, shellac wax, lignite wax, stearic acid and zinc stearate. For making W/O polishes, wax stock is then emulsified with white mineral spirit containing little ammonia or an amine and a mild abrasive.

Shellac wax has also been utilized in manufacture of radio condensers because of its high melting point. Radio condensers require waxes of a more exacting specification than do stout electrical conductors or ordinary size wire. Condenser in the small radio set in service becomes readily heated, therefore necessitating the use of a wax that will withstand at least 160ºF (~71ºC) of heat without softening or partially melting. Miniature assemblies require even higher melting point waxes. Waxes such as shellac wax, esparto wax, candelilla wax, and fibre wax, when plasticized by an adequate amount of softer wax of high melting point, are suited for the purpose.

Warth (1956) prepared a potting compound of high dielectric strength and superior flowing properties compared to wax resin or wax polyethylene compounds. The compound consisted of shellac wax 30, microcrystalline wax (M.P 77°C) 60, and polyethylene wax (M.P. 97° to 106°C) 10 parts. The blended wax had a M.P. of 96.7°C and a penetration value of 100 g (5 sec 25°C) of 10.5°. It was resistant to moisture vapour, very cohesive, of good tensile strength, and retained its flexibility at very low temperature. A potting compound of thermal resistance up to 105° to 115°C was reported having composition shellac wax 28, microcrystalline wax (M.P. 170 °F) 61 and polyethylene wax 11 parts.

Shellac wax has been utilized in making of finishing waxes for boot-soles, because of its hard and lustrous nature. Alkaline solution of shellac was used in preparing liquid finishes. Liquid finishes were also prepared from shellac dissolved in an organic volatile solvent, containing a small amount of carnauba and other waxes. Shellac wax has also been used in making shoe pastes. Following formulations have been reported:

Table 4.6 Formulations of coloured hard shoe cream of German origin

Wax	Shoe Cream (%)			
	A	B	C	D
Gersthofen wax OP"	6.5	22.0	-	-
Gersthofen wax CR"	12.8	-	16.5	14.0
Montan wax	25.6	26.0	24.5	22.0
Shellac wax	1.6	-	2.0	5.0
Gersthofen wax BJ"	-	-	3.5	6.0
Oil soluble color	9.5	13.0	11.5	11.0
White ozocerite	6.0	4.0	5.0	7.5
Paraffine (50/52°C	38.0	35.0	37.0	34.5
Total	100.0	100.0	100.0	100.0
Wax to solvent ratio	1:3	3:4	2:3	2:1

- Carnauba wax 11, raw montan wax 20, shellac wax 16, double refined montan wax 4, nigrosine base 5 with stearine 10, ozocerite 2, and paraffin (M.P. 50 to 52°C) 32 parts. The proportion of wax to solvent is 1:3 to 4.
- Carnauba wax 20, shellac wax 22, nigrosine base 3 with raw montan wax (and olein) 9, ozocerite 3, and paraffin (M.P. 50° to 52°C) 43 parts. The proportion of wax to solvent is 1:2.5.
- Carnauba wax 6, raw montan wax 33, shellac wax 4, yellow beeswax 3, nigrosine base 3.3 with stearine 6.7, paraffin (M.P. 50° to 52°C) 44 parts. The proportion of wax to solvent is 1:2.5 to 3.

Warth (1956) reported formulations of coloured hard shoe creams of German origin (Table 4.6) having following compositions:

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5

Physical Properties of Lac

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NATURAL RESIN SHELLAC is a hard and brittle solid. It transforms from solid to liquid state, when heated. Shellac, is practically odourless at normal temperature but gives out a characteristic smell on heating or melting, which is attributed to the presence of an odoriferous principle. Colour plays an important role in marketing of seedlac/shellac. Superior grades are light yellow and fetch more money; inferior grades range from deep orange brown to almost dark.

Specific gravity

Lac has been found little heavier than water. Specific gravities of different forms of lac have been studied by a number of workers (Bose *et al.*, 1963). Specific gravity of stick-lac has been reported 1.0. The value for seedlac (1.13 to 1.15) and bleached lac (1.196 to 1.217) were found similar. Comparatively wide variation has been noticed in the reported values of shellac (1.035 to 1.214).

Refractive index

This is used for identification and purity judgment of materials. Stick-lac has been found to possess higher value (1.5488) compared to other forms of lac, *e.g., kusmi* seedlac (1.52) and shellac (1.513 to 1.5295). No appreciable variation has been noticed in the values for *kusmi* and *palas* strains of shellac as well as for dewaxed variety or darker garnet lac. Bhattacharya (Bose *et al.*, 1963a) used an Abbe refractometer for a detailed study of refractive index of shellac at different temperatures. The temperature coefficient of refractive index was found $1.5\text{-}2.0 \times 10^{-4}$ between 40° and 50°C and 4.2×10^{-4} above 50°C. A plot of refractive index vs. temperature revealed softening range of shellac at 40 to 50°C.

Specific heat

Bhattacharya (1940) has reported that specific heat of seedlac (0.40-0.41 cal/g/°C) and shellac (0.36-0.37) does not depend on the host trees

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[1] Ex Principal Scientist

(*kusum, palas, khair*). Specific heat of seedlac, soft resin (0.48) and shellac wax (0.43) and heat hardened resin (0.34) possess a little lower value compared to shellac. Specific heat of lac has been reported (Srivastava, 1958) to vary slowly in temperature range 20° to 40°C (0.33 to 0.40), a rapid rise was noticed thereafter attaining a value of 0.71 at 75°C and again a fall was noticed with further rise of temperature. Rahman *et al.* (1970) noticed no appreciable change in specific heat (0.625 to 0.621) for seedlac stored up to 1 to 2 years. A little lowering in value was observed for seedlac stored beyond 2 years. Banerjee *et al.* (1970) studied variation of specific heat of bleached lac (wax-free and wax-containing) at 10° to 100°C, which was different from seedlac and shellac. The plot of specific heat vs. temperature showed two maxima around 25 and 50° to 60°C, unlike maximum around 70°C observed for seedlac/shellac. Specific heat of shellac was found similar to those of other plastics, pyroxyline (nitrocellulose plastic, 0.34-0.38), phenolic resin (0.33-0.37), *gatta percha* (0.402), vulcanized rubber (0.415) etc. The value for shellac wax was found lower than paraffin wax (mineral wax, 0.69), bees wax (0.477).

Thermal conductivity

Lee (Bose *et al.*, 1963b, c) first measured thermal conductivity of shellac in 1892 and reported the value of 2.5 mw/cm/°C. The thermal conductivity of shellac and a few modified shellac moulded compositions Bhattacharya (1942). The value for shellac was in agreement with that obtained by Lee. The value was found of the same order as of paraffin, asbestos and paper, indicating that heat dissipation by conduction through these materials is similar (Bhattacharya, 1942). Shellac- based moulded compositions possess thermal conductivities similar to those of phenol-formaldehyde compositions. Thermal conductivities for shellac-butylated-melamine-formaldehyde compositions (moulded discs) were less than that of shellac probably due to the moisture present in the discs during sample preparation (Lakshminarayanan and Gupta, 1974).

Some other parameters

Samsoen (Bose *et al.,* 1963c) determined cubic coefficient of thermal expansion of shellac. An abrupt change in value was noticed at 46°C. Considerable shrinkage takes place above 46°C and a very little below this. The low thermal expansion was considered valuable information for moulding work, especially, for its erstwhile application in gramophone record industry, facilitating removal of records from moulds at 40°-50°C without any appreciable shrinkage.

Researchers also studied velocity of sound in lac resin. Smoluchowski (Bose *et al.,* 1963d) investigated velocity of sound at different temperatures in a sample of white lac (presumably bleached lac). A value of 970 m/sec was determined at 19.4°C; rise in temperature caused a decrease in the value (762 m/sec at 40°C). Stefan reported 1320 m/sec in a sample of sealing wax (undefined composition).

Verman (Bose *et al.,* 1963d) determined values of elasticity, which is an important property for plastic materials, from measured value of velocity of sound employing,

$M=V^2D/G$

where, M, modulus of elasticity in g/cm^2;V, velocity of sound in cm/sec; D, density in g/ml (1.2), and G, acceleration due to gravity in cm/sec^2. The modulus of elasticity was 12,450 and 7,100 kg/cm^2 at temperatures 8.7° and 40°C.

Houwink (Bose *et al.,* 1963d) made an experimental determination of modulus of rigidity of T N shellac, which was 26,000 kg/cm^2 at room temperature. A higher value of 26,000 kg/cm^2 was obtained by heat curing of shellac at 110°C for 24 hr. The above value corroborated well with values obtained earlier.

Flow/fluidity

Determination of flow either by ASTM or Victor process is used by the industry for ascertaining freshness of seedlac or shellac. [In the polymer industry, knowledge of 'melt flow index' is generally used for moulding work. The same has not yet been determined for shellac]. Fresh shellac may possess a very high value of flow of 90 to 95. Seedlac generally possesses a low value of flow because of impurity. Flow of shellac has always been noticed higher than seedlac. Generally, seedlac or shellac having a minimum flow value of 50 is workable for utilization for application or making different lac-based formulations. Flow of seedlac and shellac has been noticed to vary with strain of lac insect crop/time of

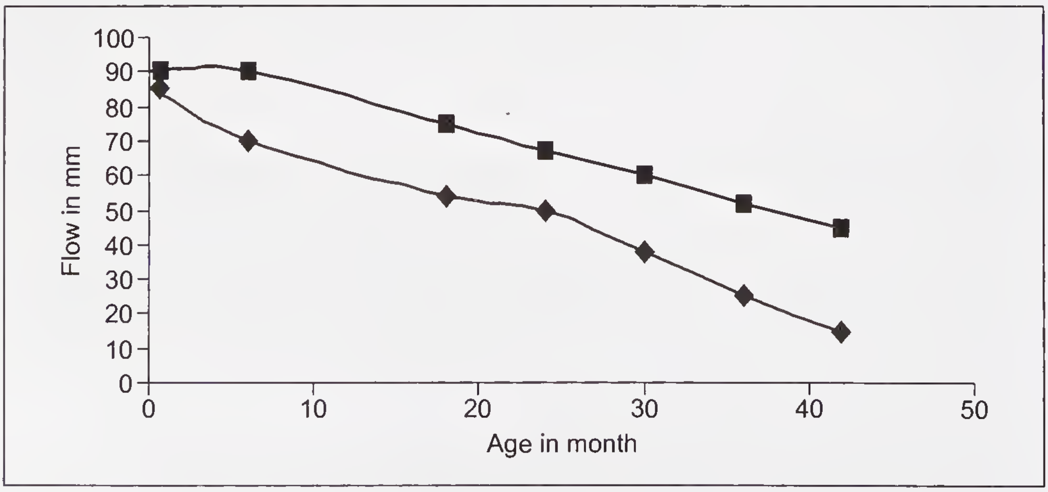

Fig 5.1 Decrease in flow with age of *Kusmi aghani* seedlac (lower) and shellac (upper) stored at room temperature.

harvesting. *Kusmi* shellac has been found to possess better flow compared to *rangeeni* shellac. Flow of seedlac and shellac has been reported to decrease with age due to polmerisation of resin molecules. (Fig.5.1). The rate of deterioration of shellac of summer crop (*jethwi*) was found rapid to winter crop (*aghani*); the rate of rainy season crop (*katki*) was found intermediate of the two.

Melt-viscosity

Knowledge of this property is useful when a material (plastic) is used for moulding purposes. Basu (1947, 1948) carried out a study on lac, its 2 major fractions and a few modified compositions with an indigenously developed Ostwald type of viscometer using mercury for causing flow of molten shellac through capillary (Table 5.1).

Table 5.1. Melt-viscosity of shellac, soft and hard resins.

Sample	Temperature °C	Viscosity in Poise(PaS)
Dewaxed shellac	80	22,505 (2250)
	85	10.063
	90	4,533
	95	2,154
Soft resin	45	1,17,912
	50	58,956
	57	20,810
	60	10,405
Hard resin	85	27,230
	90	7,527
	95	2,788
	100	1,316

Lowering of viscosity at higher temperature indicated conformational changes in molecules through micelle formation. Melt-viscosity of esters and acetyl derivatives of shellac were studied and it was inferred that both hydroxyl and carboxyl groups of shellac molecules took part in micelle formation (Basu, 1947). Basu (1948) concluded that presence of plasticisers, lowered activation energy for viscous flow; plasticisers miscible with shellac increase viscous volume and those that are incompatible lower it.

Study on flow parameters of polymer/resin solutions and melts provides information useful for designing formulations/products of commercial interest and rheological studies on polymers/resins are important in regard to their process ability and to understand their flow behaviour. The flow behaviour of polymers/resins in concentrated solutions is different when compared with dilute solutions. In concentrated solutions, entanglement of polymer molecules takes place resulting in three-dimensional network structure. Knowledge of rheological parameters is also of practical and fundamental interest for understanding behaviour of resin-based formulations.

Goswami *et al.* (2003) recently have studied melt-viscosity of shellac at different temperatures and time and investigated the flow curves. The solution viscosity of shellac and a few shellac-based varnishes by a cone and plate Haake rheometer revealed information regarding yield stress (minimum force required for initiating flow) and thixotropic properties of shellac and shellac-based materials. Such information will be useful for developing shellac-based moulded articles and shellac-based varnish compositions. Viscosity curve of (molten) shellac was obtained by Goswami *et al.* (2003) and is shown in Figs. 5.2 and 5.3. A decrease was also observed in melt-viscosity of shellac with an increase in temperature (Fig. 5.3). This suggests conformational changes in shellac molecules with rise in temperature.

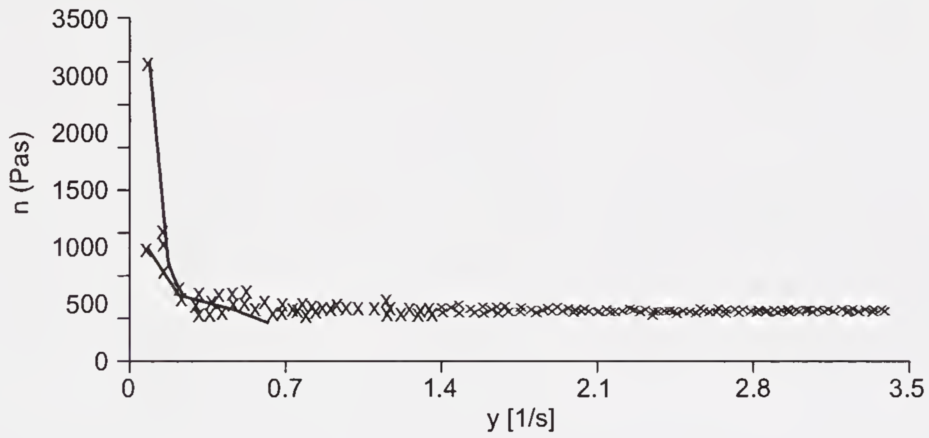

Fig. 5.2 Viscosity curve of molten shellac at 110°C

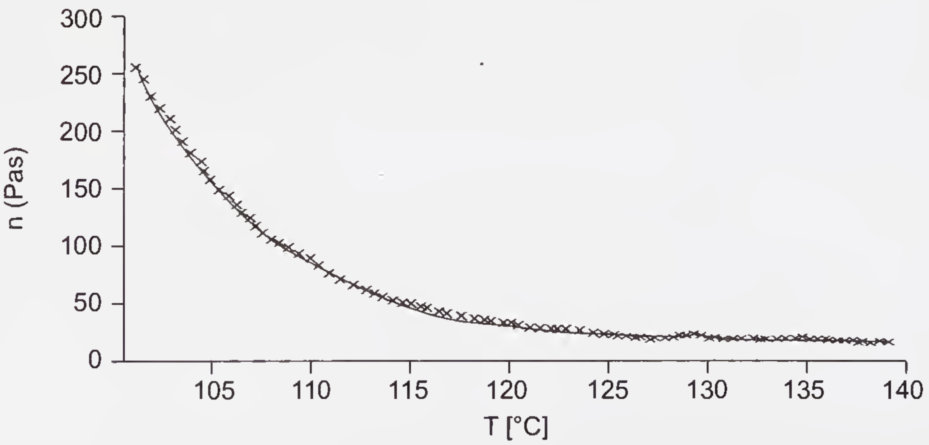

Fig 5.3. Variation of (melt) viscosity of shellac with temperature

Rheologial studies of coatings also throw light on levelling, sagging, brush ability. Levelling is the ability of the coating to flow laterally and diminish thickness of the adjacent areas of a coating. This property affects smoothness, gloss, colour and mechanical behaviour. Levelling also involves changes in surface tension due to solvent loss due to evaporation and/or reaction and its influence by materials' yield stress and viscosity. Sagging is undesirable flow of a coating down to vertical surface. Whether a coating will sag or not will depend on its thickness and its viscosity at low shear rates. For a coating to be free from sagging, the product of its density (ρ), gravitational constant (g) and its thickness must not exceed yield stress ($\rho gt < \tau_o$).

The steady viscosity was observed for solution of shellac when rate of shear was increased up to 150/sec. Viscosity (η) and shear stress (τ) were stable with time for rate of shear 150/sec or more. Solution of shellac has exhibited both shear thickening and shear thinning properties. Viscosity of shellac solution increased with rise in shear rate of 150/sec. Then viscosity showed little decrease beyond 150/sec, the decrease noticed was not much (Goswami *et al.,* 2003).

Molecular weight

The average values of molecular weights of shellac, soft and hard resins, also of bleached lac are 1006, 949, 478 and 1800 respectively (Basu *et al.,* 1963e). Palit and Bhattacharya (1939) recorded molecular weights of hard and soft resins as 1918-1932 and 535 respectively from acid value and basicity. Basu (1948) obtained a similar range 1801-1896 and 481-490 for hard and soft fractions using osmotic pressure method. Gupta and Bhattacharya (1969) determined molecular weights of shellac, its hard and soft fractions employing method of Rast, acid value, viscometry and vapour phase osmometry methods. The molecular weights of shellac, decolourised lac, hard and soft fractions were 1090, 1060, 1830 and 588 respectively (Gupta and Bhattacharya, 1969). Taking into account results of different researchers the average molecular weights of shellac, hard and soft fractions are accepted, in general, as 1000, 1900 and 500 (Bose *et al.,* 1963e).

Softening and melting points

Non-crystalline materials do not possess sharp melting points. Natural resin shellac behaves similar to amorphous materials. On heating, shellac softens and transforms from solid to liquid phase. Shellac being natural contains different constituents, so its softening and melting depend on the source. Tamman (Bose *et al.,* 1963f) found softening between 30.5 and 56.5°C. Nagel (Bose *et al.,* 1963f) obtained a comparatively higher range for shellac (80° to 90°C) by adopting a method in which mercury falls through soft and molten lac in tapering tube closed at one end. Hoseason and Klug (Bose *et al.*, 1963f) found melting of different grades of stick-lac as 79.5° to 83°C. Rangaswami (Bose *et al.* 1963) reported melting at 85° to 86°C. Higher melting was reported for certain grades of lac (Anon., 1937). From an exhaustive study made at this Institute, the softening range of stick-lac and shellac is taken as 65° to 70°C and the melting points are about 10° higher.

Melting of different forms of lac: Goswami and Walker (1993) first studied melting of shellac, its hard and soft fractions at different rates of heating employing Differential Scanning Calorimeter. The higher rates of heating were observed to yield higher melting temperatures. It was found that a heating rate of 20°/min is optimum for obtaining melting temperatures, which corroborate with data obtained by other workers. Goswami and Saha (2000) studied melting of different forms of lac by DSC thermograms (Fig.5.4) that revealed melting of lac (stick-lac, seedlac and shellac) a two-step process, as two melting peaks were observed between 55°-57° and 72°-74°C. The resin portion melts first, followed by melting of shellac-wax (the peak at higher temperature). Conventional method, however, gives only one melting temperature around 65°-75°C. Dewaxed lac and dewaxed bleached lac give only one peak at temperature around as for resin portion (Fig.5.5). Melting profile of lac by D.S.C. can be a quick and convenient method for identification of presence of wax than chemical method. Thermograms of *kiri* revealed relatively smaller peak for resin and a more prominent peak for the wax. The melting of *kiri* was found to occur at a relatively higher temperature than native shellac. The reason might be that the material present within the filter press undergoes partial polymerization yielding, relatively higher melting temperature.

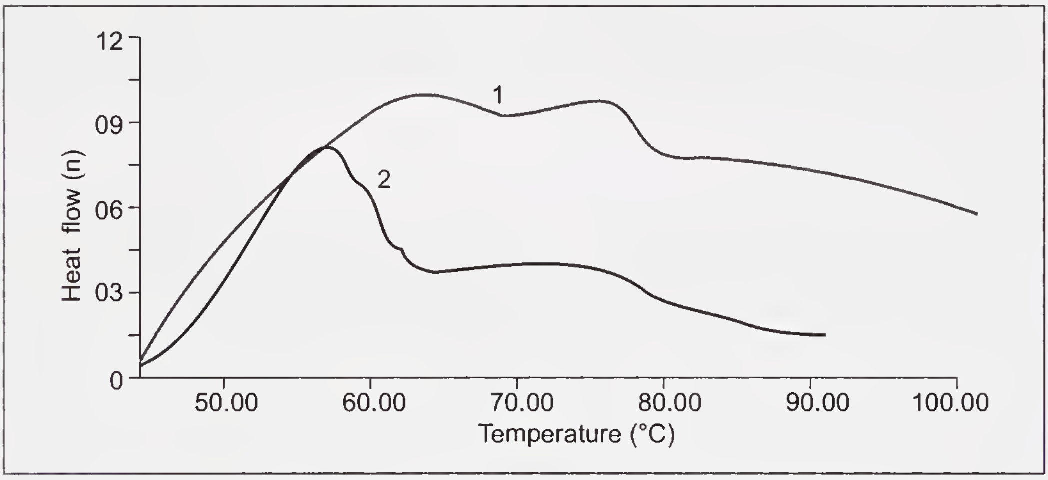

Fig. 5.4 Melting profiles of shellac of two different melting temperatures.

Melting of polymerised lac: Melting profile (by DSC) of heat-polymerized

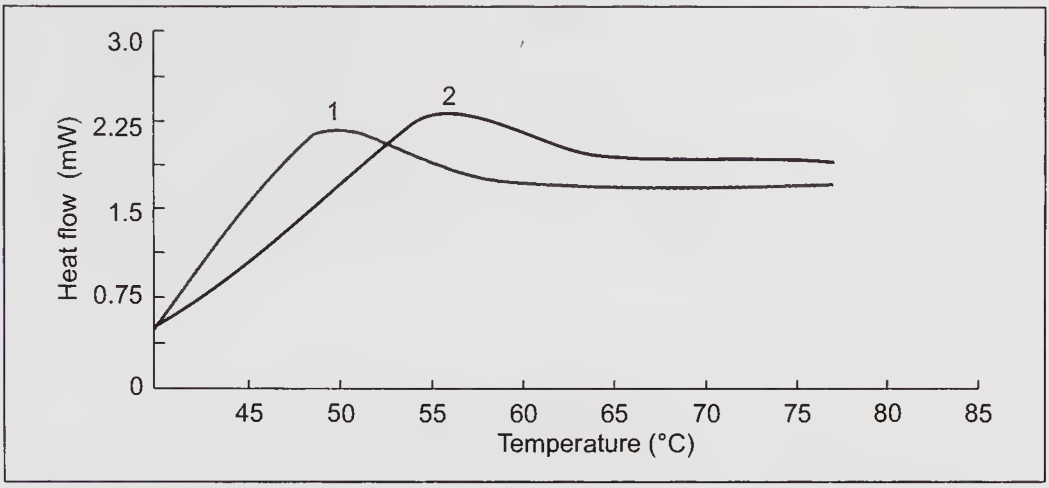

Fig 5.5 DSC thermograms of (1) dewaxed lac and (2) dewaxed bleached lac. The absence of peak due to wax around 72°C may be noticed.

lac was found different from polymerized lac obtained due to aging (Goswami and Saha, 2000). Lac resin (seedlac, shellac) polymerized through aging did not show any peak due to the resinous portion (Fig.5.6), which indicate cross-linking of resin molecules. The peak due to wax was, however, present. Heat polymerized lac (heated for 90 min above HPT) showed a small peak for resin portion (Fig.5.7), indicating that by heating beyond polymerization time, resin molecules do not become fully polymerized. This result suggests that lac resin is not a truly thermosetting type. Small multiple peaks were observed in the position for peak for wax which indicate degradation of constituent long chain alcohols present in the wax. Heat polymerized lac was also found partially soluble (qualitative observation) in alcohol (Goswami and Saha, 2000).

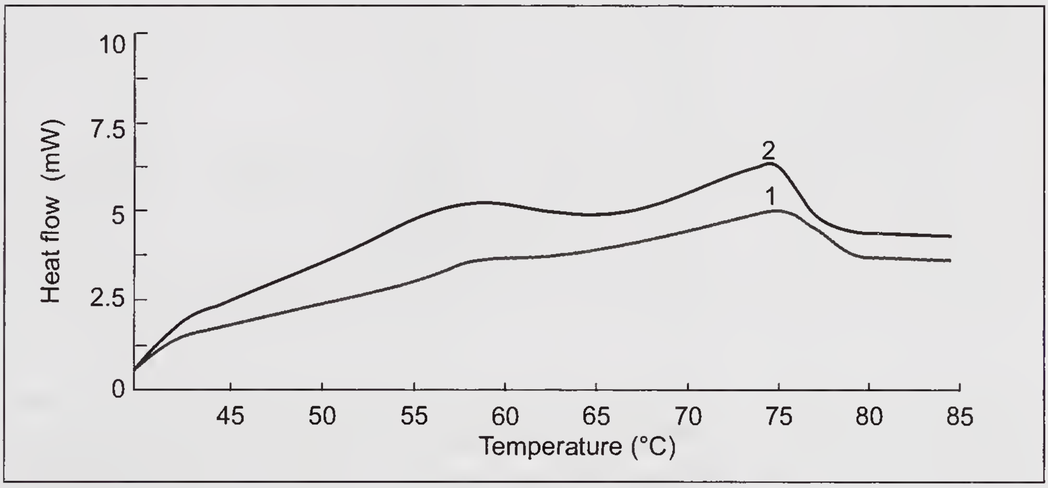

Fig 5.6 DSC thermograms of polymerized (1) seedlac and (2) Shellac due to ageing.

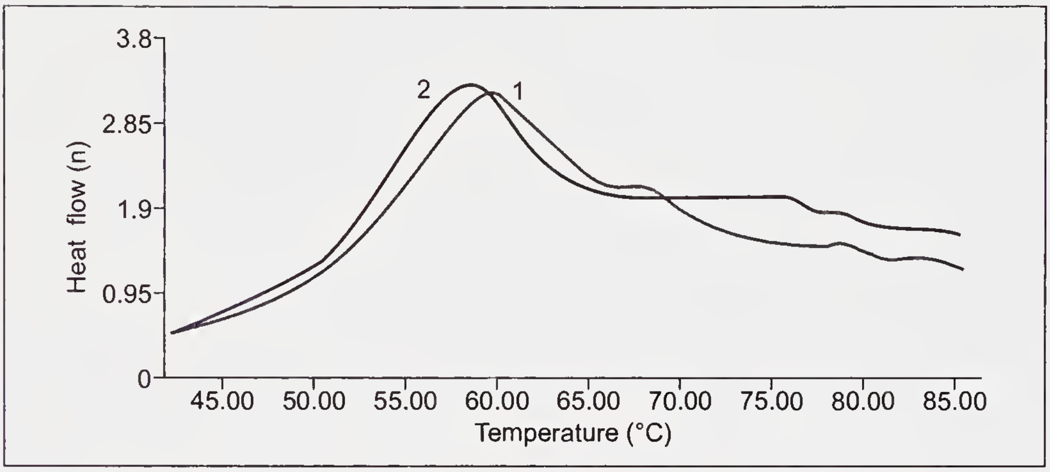

Fig. 5.7 Melting profiles of heat polymerized (1) seedlac and (2) shellac.

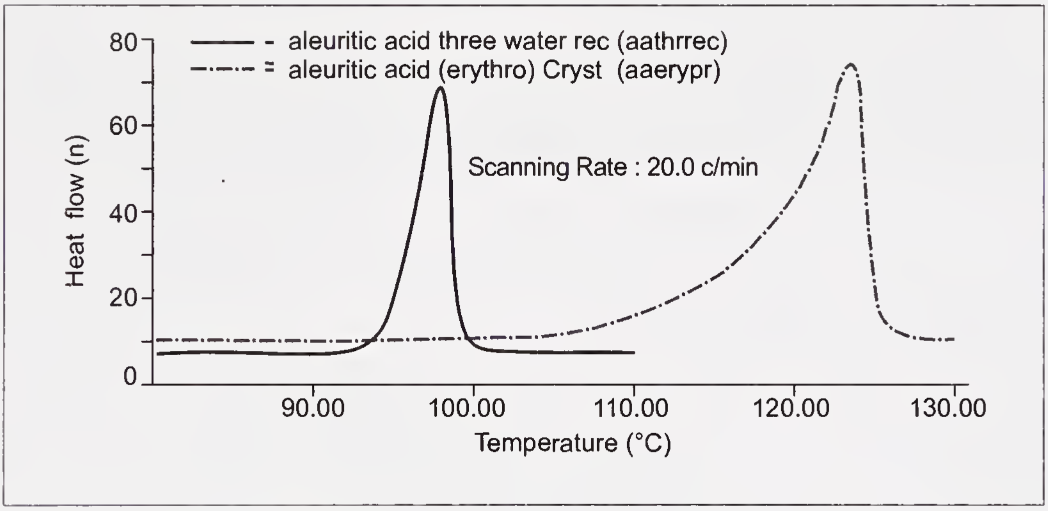

Fig 5.8 Melting profiles of *threo*- (left) and *erythro*-aleuritic acid (right) by D.S.C.

Melting of soft and hard fractions of lac: According to Goswami and Walker (1993) by DSC, wax was not separated from the fractions. Hard fractions showed two melting peaks around 78° and 87°C. Soft fraction revealed presence of peaks around 48°, 56° and 63°C respectively; indicating soft resin contains more fractions than those present in the hard fraction.

Melting of aleuritic acid

Melting profiles of *threo*-aleuritic acid and a derivative were investigated employing DSC (Goswami *et al.*, 1997). Crystalline pure *threo*-aleuritic acid (crystallized from boiling water) gave a sharp peak at 97.7°C and onset temperature at 94.9°C, compared to 100° to 101°C determined by conventional method; *erythro*-aleuritic acid gave a melting peak at 123.2°C (Fig.5.10) and onset was found at 118.8°C. Non-crystalline samples produced melting peaks and onset temperatures lower than those of crystalline compounds. These also yielded more peaks. *threo*-Aleuritic acid crystallized from ethyl acetate yielded relatively impure products (when compared with boiling water) and former gave more peaks. Higher values of melting temperatures obtained by conventional method are owing to: (*i*) a very small quantity (a few particles) of material taken, (*ii*) higher rate of heating applied, (*iii*) melting realized when a substantial quantity of material has undergone phase change, and (*iv*) human error.

Glass-transition and melting temperatures of shellac and a few other natural resins

It is known that natural resins do not show a definite melting point, fusion occurs gradually, when heated. The transition from solid to liquid occurs through a glassy state. The glass-transition temperatures of shellac, its hard and soft fractions were found almost identical to their softening temperatures (Goswami, 1980) Table 5.2. For polymers, on a molecular

Table 5.2. Glass transition and melting temperatures of shellac, its constituents and few other natural resins (Goswami, 1980)

Resin	T_g (°K)	T_m (°K)	T_g / T_m
Shellac	313	343	0.91
Hard lac resin	323	353	0.92
Soft lac resin	283	313	0.90
Manila copal	343	373	0.92
Mastic	345	376	0.92
Dammar	373	393	0.95
Pontianac	360-408	408-434	0.88-0.94
Sandarac	373-403	408-423	0.91-0.95
Kauri	378	403	0.94
Congo	360	401	0.898
Manila Macassar	353-361	388-401	0.91-0.90
Manila Philippine	359	398	0.90
Manila Singapore	367	399	0.92
Batu East India			
Scrapped	385-405	441-453	0.87-0.89
Dust	404	438	0.92
Pale East India Macassar			
Bold-Hiroe	374-385	400-429	0.94-0.95
Dust-Hiroe	389-395	413-429	0.94-0.90
Pale East India Singapore			
Bold	382-401	420-429	0.91-0.93
Dust	387	423	0.91
Accroides	348-358	383-407	0.91-0.8

scale, polymer chains are ascribed to acquire considerable mobility above softening point or glass-transition temperature (T_g). Boyer (1977) showed that T_g/T_m ratios of 55% of all polymers lie in the band 0.667 +/- 0.05. Since shellac and many natural resins are being used in the paint and varnish industries along with polymers for many years and shellac is considered polymeric, knowledge of the T_g, T_m and T_g/T_m ratios of shellac and other natural resins seemed helpful in their use in moulding application.

T_g of shellac was investigated by D.S.C. thermograms (Goswami and Walker, 1993, and Goswami and Saha 2000), dielectric (Goswami, 1979), specific heat, refractive index etc. The value (40°C) determined by different methods was found identical (Goswami, 1979), Table 5.2. T_g/T_m ratios of natural resins fall between 0.88 and 0.95. Beaman (1952) obtained a range of 0.5 to 0.78 for T_g/T_m for materials other than polymers. Thus, T_g/T_m ratios of natural resins have been found different than other materials. This suggests that natural resins belong to a different class of materials. A satisfactory interpretation of the observed data is difficult, because natural resins are chemically ill-defined.

X-ray diffraction

Clarke (1926) first attributed shellac as an amorphous substance from X-ray diffraction study, whereas von Narey-Szabo (1927) obtained five distinct rings at 6.37, 5.31, 5.03, 4.88 and 4.84 ′ and classified shellac as crystalline substance. Krishnamurty (1929) classified it as an amorphous substance and obtained two rings at 11 and 4.76 ′. Lakshminarayanan and Gupta (1975) obtained three halos at 2.48, 4.93 and 11.33 ′ in X-ray diffractogram of shellac and revealed it possessing 17.8% crystallinity. They observed an increase in crystallinity up to 35.6% when shellac was blended with 30% melamine resin. An inspection of D.S.C. thermograms of shellac revealed its amorphous nature and flat maxima indicated its many constituents. Basu (1948) studied diffraction pattern of hard resin and obtained two diffused rings at 10 and 4.21 ′. First was attributed to miceller aggregation of hard resin molecules, similar to cybotactic, and the second was due to long-chain molecules having more than four carbon atoms. Pan (1976) studied X-ray diffraction pattern on the orientation of magneto-electret forming shellac-wax, which showed preferred orientation, and was explained by assuming existence of cybotactic groups in liquid state at the formation temperature.

Optical rotation

Specific rotation [á]$_D^{25}$ of shellac, bleached lac, hard and soft resins were found +60.71, +59.29, +54.83 and +63.60 respectively by Sharma and Sreenivasaya (1944), who further observed shellac to be dextrorotatory.

Solubility

Fresh seedlac and shellac are readily soluble in its common alcoholic solvents, this characteristic may be adopted for determining their freshness (Table 5.3). Solubility decreases with ageing.

Solubility behaviour of shellac can be explained by solubility parameter and cohesive energy density (Table 5.3). The cohesive energy density is

Table 5.3. Solubility of lac in different solvents

Solvent	Boiling point (°C)	Solubility Parameter (δ)	Solubility of		
			Stick-lac	Seed-lac	Bleached lac
(1)	(2)	(3)	(4)	(5)	(6)
Hydrocarbons					
Aliphatic					
Cyclohexane	156.7	8.2	S	FS	FS
Cyclochlorohexane	80.7	-	I	FS	FS
Petroleum ether	78	-	FS		
Aromatic					
Benzene	79.7	9.15	I	I	I, SW
Nitrobenzene	210.85	10	I, SW	I, SW	SS
Toluene	110.7	8.9	I	I	I, SW
Xylene	142.6	8.8	I	I	I, SW
Halogen compounds					
Bromo benzene	156.15	10.0	I	I	I, SW
Amyl chloride	137	8.3	S	S	S
Chloroform	61.2	9.3	I, SW	I, SW	I, SW
Carbon tetrachloride	76.74	8.6	I	I	I
Ethylene dichloride	83.8	9.8	I, SW	I, SW	I, SW
Ethylene chlorohydrin	128	12.2	S		
Monochlorohydrin	213-228			SS	
Dichlorohydrin	174-176			S	
Epichlorohydrin	117			I	
Dichloroethane	83.7			I	
Trichloroethylene	86-87.5	9.2		I	
Chlorobenzene	132	9.5		I	
Dichlorethylether	178			I	
Hydroxyl compounds					
Water	100	23.2	I	I	I
Glycerol	290	16.5	I	I	I
Methanol	64.57	14.5	S	S	S

S soluble; I insoluble; FS fairly soluble; SS slightly soluble; SW swells [from Bose *et al.*, 1963; Duran, 1933; Brandrup and Immergut, 1966]

(Continued to p. 74)

(Table 5.3. Continued from p. 73)

(1)	(2)	(3)	(4)	(5)	(6)
Ethanol	78.4	12.7	S	S	S
n-Propyl alcohol	97.3			S	
Isopropyl alcohol	82.85	11.5	S	S	S
Amyl alcohol	137	10.9	S	S	S
s-Butyl alcohol	99.8	10.8	S	S	S
Ter-Butyl alcohol	83	10.6	S	S	S
Benzyl alcohol	200	12.1		S	
Acetadol			I		
Citronellol	222		SS	SS	SS
Diethyl carbitol	116		S	S	S
Iso-Butyl carbitol	131.4		S	S	S
Sec-Butyl carbinol	128.7		S	S	S
Diacetone alcohol	164		S	S	S
Methylpropyl carbinol	118.5		S	S	S
Dimethyl ethyl carbinol	102.5		FS	FS	FS
Geraniol	230		FS	FS	FS
m-Cresol	202.7	10.2	S	S	S
Furfural alcohol	168-172	12.5		S	
Tetrahydro furfurol alcohol	178-181			S	
Ethylene glycol	197.37	15.7	I	I	I
Diethylene glycol	245	12.1	S	S	S
Dioxane	101.1	10.0		S	
Acids					
Acetic acid	118.1	10.1	S	S	S
Butyric acid	162.3	10.5	S	FS	FS
Formic acid (85%)	100.47	12.1	S	S	S
Palmitic acid	271.5		I	I	I
Lactic acid	119		FS	FS	FS
Propionic acid	104.7	9.9	S	S	S
Esters					
Amyl acetate	148	8.45	I	I	I
Methyl acetate	57.1	9.6		I	
Ethyl acetate (85%)			FS	FS	FS
n-Butyl acetate	125.1	8.55	I	I	I
Diethyl carbonate	125.8	8.8	I	I	I
Diethyl phthalate	290.4	10.05	I	I	I
Iso-Butyl propionate	137		I	I	I
Ethyl lactate	154.5	10.0	S	S	S
Ethyl oxalate	186.1		I	I	SS

S soluble; I insoluble; FS fairly soluble; SS slightly soluble; SW swells [from Bose *et al.*, 1963; Duran, 1933; Brandrup and Immergut, 1966]

(Continued to p. 75)

(Table 5.3. Continued from p. 74)

(1)	(2)	(3)	(4)	(5)	(6)
Ethyl oxyburate	145.5		FS	Fs	FS
Ethylene diacetate	186.7		I		
o-Nitraniline in ethyl acetate	284.1		SS		
Ethylene glycol ethyl ether acetate (distilled)	154		I	I	SS
Glycol monoacetate	181			I	
Glycol diacetate	186-190			I	

S soluble; I insoluble; FS fairly soluble; SS slightly soluble; SW swells [from Bose *et al.*, 1963; Duran, 1933; Brandrup and Immergut, 1966]

numerically equal to potential energy of 1 cc of the material. Solubility parameter is defined as the square root of the cohesive energy density, which is the most useful parameter for predicting solubility of any material in a solvent. If a material (resin/polymer) and a series of solvents have similar polarity, resin becomes soluble in these solvents whose cohesive energy densities (and solubility parameter) are not different from its own. Solubility parameter of shellac has been determined by solubility behaviour (Khanna, 1970), mid-point of ä range (Banerjee *et al.*, 1982), structural contribution technique (Banerjee *et al.*, 1982), intrinsic viscosity (Banerjee *et al.*, 1982) method and Hansen's three-dimensional approach (Goswami *et al.*, 2003). The value of solubility parameter of shellac determined by last 2 methods were similar [11.2 $(cal/cc)^{0.5}$]. Solubility parameter of aleuritic acid free gummy mass was observed 10.6 (Goswami and Prasad, 2000).

Lac resin from different lac- insects

The lac insects (77 species) have been reported out of which *Kerria lacca* (*kerr*), *Kerria chinesis* and *Kerria* sp. are commercially exploited for lac cultivation (Varshney, 1990). *Schleichera oleosa, Buteau monosperma* and *Ziziphus mauritiana* are main hosts of Indian lac insect. *Kerria chinesis* is used for lac cultivation on *Samanea saman* in Thailand. *Cajanus cajan* and *Protium serratum* are main hosts for lac cultivation in Vietnam. Bose *et al.*(1963g), Sarkar and Srivastava (2001), Rangaswami and De (1944) and Lu Fuji (1991) reported that lac resin secreted by different insects differ in physico-chemical properties. Saha (1995) reported significant differences in certain physico-chemical properties of lac resins obtained from the above three different species (Table 5.4). The resin obtained from *Schleichera oleosa* was superior to other resins in regard to some industrially important parameters *e.g.,* flow (highest), heat polymerization time (longest) and colour index (lowest). The flow and HPT values observed for both Thai and Vietnamese lac were considerably

Table 5.4. Physico-chemical properties of lac resins obtained from different species of lac insects*

Properties	India *Kerria lacca (kerr)*			Thailand *K.chinensis*	Vietnam *K.sp.*	
	Schleichera oleosa	*Buteau monosperma*	*Ziziphus mauritiana*	*Samanea saman*	*Proteum serratum*	*C.cajan*
Flow (mm)	62	48	52	26	35	30
Heat polymerisation time (min)	70	65	65	45	44	56
Colour index	10	12	12	33	27	39
Wax (%)	5.5	5.8	5.6	2.8	3.3	4.5
Melting point (°C)	78	79	78	82	83	86
Acid value	67	66	66	80	80	79
Saponification value	223	222	222	236	229	227
Hydroxyl value	254	250	250	-	-	-
Ester value	156	156	156	156	149	148
Carbonyl value	22	23	23	34	34	37
Iodine value (Wij's method)	15	14	15	16.6	16.8	17.1
RF values of major spots in TLC	3 spots (0.11, 0.35, 0.83)	3 spots (0.12, 0.37, 0.82)	3 spots (0.13, 0.33, 0.80)	4 spots (0.12, 0.19, 0.52, 0.64)	4 spots (0.12, 0.19, 0.52, 0.64)	-
Conductivity at 100 kHz (ìmho/cm)	4.5	5.2	2.1	8.1	3.8	-

*Saha, 1995.

lower to corresponding to Indian lac resins. Colour was observed darker for Thai and Vietnamese lac when compared with Indian lac. TLC data revealed that both Thai and Vietnamese lac contained more number of constituents. Comparative studies .on the changes in different physico-chemical properties after one-year of storage of seedlac and shellac of Indonesia, Thailand and India revealed that Indian seedlac and shellac are better compared to others for flow, heat polymerization time, colour index, gloss, and bleach index (Anon, 2005-06).

Effect of storage on different physical parameters of lac

Deterioration in qualities of lac with storage is a common problem. Lac cannot be stored for long at room temperature, owing to rapid degradation in its physico-chemical characteristics takes place, due to polymerization of resin molecules. Flakes of shellac coalesce and form lumps (commercially known as blocking) under ambient conditions of storage. This 'lump' formation, also known as matting (Anon., 1963) does not cause any major change in properties of shellac for short periods of storage. However, fluidity (flow) of resin is adversely affected over storage even at room temperature. Increase in room temperature, humidity and also pressure enhances blocking and formation of hard slabs which can be crushed only with difficulty.

Rangaswami and De (1944) studied the changes in different physical properties of stick-lac, seed-lac and shellac and of two major commercial crops of lac *baisakhi* and *kusmi*. These were stored under normal room temperature and also in air-conditioned godowns maintained at 25°C through Air Conditioners and relative humudity 60%. The observations are as follows:

- An increase in total impurities in stick-lac on aging, independent of nature of storage.
- Increase in both cold and hot alcohol insoluble in first 2 years of storage but a rapid increase was observed thereafter for seedlac stored under normal room temperature. The corresponding effect was negligible even after storage for more than 2 years and 6 months for *kusmi* and *baisakhi* seed-lac in storage having Air Conditioner.
- Both seed-lac and shellac became darker in storage under room temperature condition (However, no appreciable change in colour index observed). Negligible colour change was observed in air-conditioned storage.
- The rate of filtration was considerably affected (reduction) in storage under room temperature. The deterioration, however, was not observed for samples stored in air-conditioned godowns.
- Storage type did not have any effect on bleaching quality of seedlac.
- Fluidity of shellac (stored in normal conditions) was badly affected; it diminished progressively with age until shellac became partially polymerized. Very little deterioration, however, was observed for shellac stored in air-conditioned godowns for even 2–3 years.
- The life under heat was adversely affected (reduced) in both types of storages but change noticed was comparatively lower under air-conditioned storage.
- Softening and melting ranges of seedlac and shellac were raised, which were found more in ordinary storage compared to those in air-conditioned atmosphere.

Consequently quality of seedlac and shellac could be maintained over longer periods, if they were stored in air-conditioned godowns. The expenses thus incurred, however, could be compensated by higher price of lac due to its better keeping quality.

Khanna *et al.* (1986) studied changes in several physico-chemical properties of seedlac and shellac undergone due to aging. Flow was found most sensitive property, which was affected due to storage. Besides, a gradual lowering was observed in life under heat, rate of filtration, dielectric strength, dissipation factor, conductivity and an increase in cold alcohol insoluble, indicating deterioration in qualities. Saha and Bhowmik (1984), and Saha (1992) studied effect of aging on stick-lac and seedlac stored in air-conditioned as well as in ordinary condition and observed the following:

- High moisture content in stick-lac is responsible for blocking *i.e.*, hard lump formation. The optimum moisture content was identified to be 4% for storing stick-lac to avoid lump formation.
- Very high and very low humidity causes rapid decrease in flow value. A relative humidity around 45% is considered ideal for storing lac at ambient condition (away from light). Mc Cullock (1943) observed that shellac becomes infusible after 175 days when kept at 75% relative humidity.
- Storage of dry stick-lac in hessian bags was found best, as the quality could be maintained over longer periods. Stick-lac retained their flow and life under heat characteristics compared to those kept in the open shed.
- Storage of seed-lac is preferred over storage of stick-lac form, as there is no advantage of storing stick-lac.
- Impurities and colour index of stick-lac resin increased with age, while these were unaffected if stored as seedlac and shellac.
- For the same stick-lac, no appreciable difference was observed in resin quality flow, life and rate of filtration whether stored as stick-lac or seedlac. However, per cent of loss in flow was lower when stored as seedlac up to 18 months of storage.
- Air-conditioned storage was definitely superior to other forms of storages. Even after 48 months, the loss in the flow value of seedlac was only 20% as against 55% when same sample was stored in room temperature.

Thus, gradual lowering in solubility in alcohol, fluidity and life under heat suggest slow polymerization of lac. The melting profiles of 13-year-old seedlac and shellac investigated by DSC also did not show any peak due to melting of resin (Fig.5.6).

Recently, Goswami *et al.* (2003-2006 and 2009) studied changes in physico-chemical properties of seedlac and shellac due to stotage at room temperature of three crops of lac. Followings are the main observations:

- Initial values of the physical constants (flow, alcohol insoluble etc.) of seedlac and shellac vary widely for different crops, time of harvesting etc. because of natural origin.
- Variation in initial values of chemical constants acid and hydroxyl values, was lesser than physical constants.
- Moisture content of seedlac and shellac should be 2% or even less before storage to avoid blocking.
- Storage of seedlac/shellac should be made in a place free from

dampness, away from light, preferably in perforated (top, side) paper cartons (3 kg pack) to avoid pressure on seedlac grains or shellac flakes to avoid blocking (observed for 4 years).

- Blocking was not observed for stick-lac (free from moisture) stored inside polybag (thickness more than 50 m) even without addition of sodium chloride.
- Seedlac and shellac treated with low concentration of an antioxidant extends storage life at least 6 to 8 months at the initial stage.
- Oxalic acid should not be added in seedlac while converting it into shellac, as it causes rapid polymerization of shellac with storage even at room temperature. Flow becomes zero within 30 months of storage (Fig.5.9). Shellac prepared without addition of oxalic acid in seedlac does not deteriorate so fast and can be stored for more than 2 years (Fig.5.10).

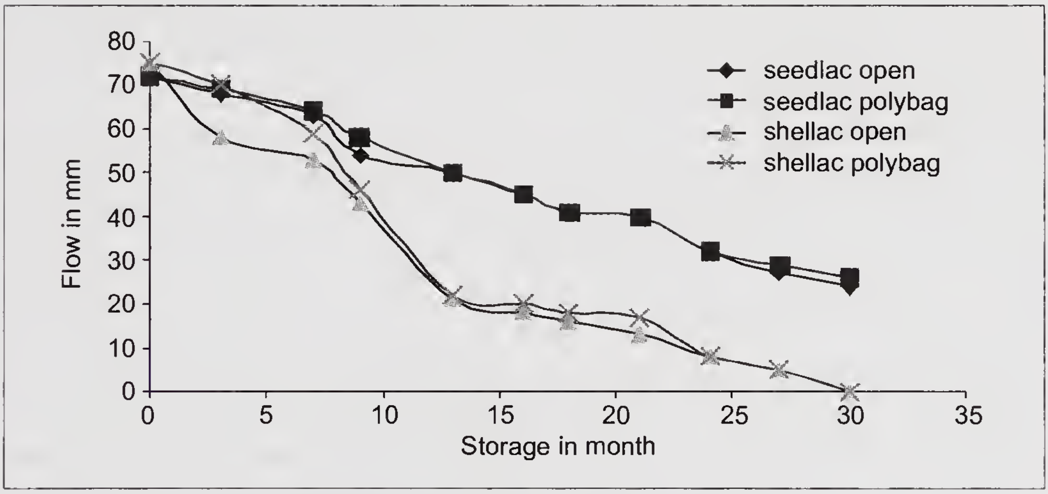

Fig 5.9 Change of flow with storage of seedlac and oxalic treated shellac. Flow of shellac reaches zero within 30 months of storage

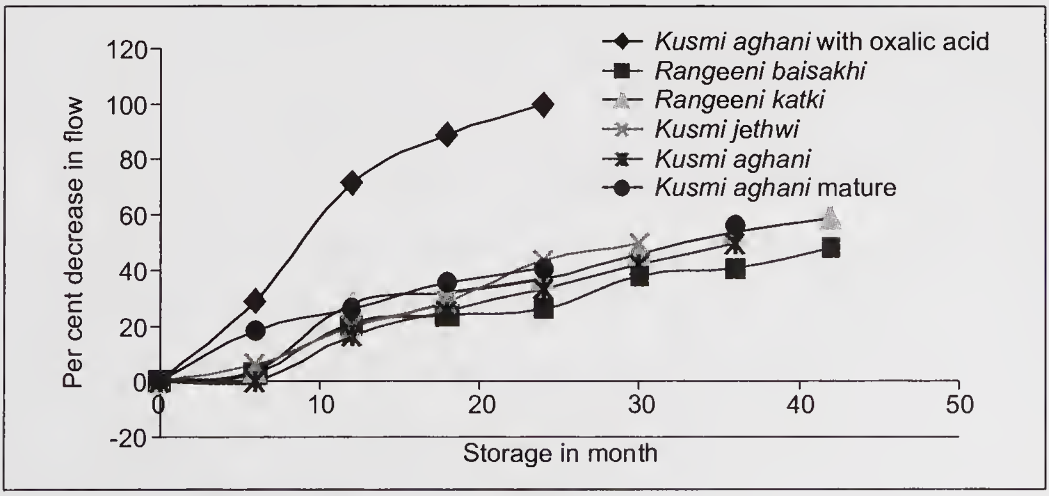

Fig. 5.10 Percentage decrease of flow of shellac treated with oxalic acid and untreated shellac. Shellac with oxalic acid attains 100% decrease in flow within 30 months of storage. Untreated shellac attained about 60% decrease in flow after 42 months of storage.

- Storage of seedlac is wiser than shellac, as and when seedlac is converted into shellac, it always gives flow more than that of seedlac. In general, gradient of decrease of flow (with age), observed of seedlac, is lower than that of shellac, indicating better keeping property of seedlac.
- Application of an antioxidant (in dilute solution) delays degradation at least by 6 months in summer crop (*jethwi)* of *kusum* and rainy crop (*katki)* of *rangeeni* lac in early period of storage. This is also a first information report.

The depolymerisation can be carried out by acid hydrolysis with 3% HCl in alcohol. Shellac obtained through aging could also be converted to original form by merely dissolving it in acetic acid or formic acid or by heating in the presence of water in an autoclave (Bose *et al.*, 1963). Nagel and Körnchem (1927) attributed change due to aging due to the presence of certain colloidal chemical forces, which tend to bring a certain number of resin molecules to form aggregates, which behave differently, when compared with original molecules. The reversal to original form is ascribed to disintegration of these aggregates under suitable conditions (Bose *et al.*, 1963). Palit (1942) indicated that pure resin molecules pass through an intermediate stage to reach insoluble stage. The intermediate product was found to be a semi-polymer (dimer) of pure resin. Palit further inferred that semi-polymer is formed through ether linkages, although no experimental evidence was obtained. Later, Saha (1992) postulated that polymerization of lac during storage under ambient conditions is photo-induced (in analogy with oxidative degradation noticed for some synthetic polymers (Gowariker *et al.*, 1998) when exposed to atmospheric conditions) and that polymerization proceeds *via* slow formation of peroxides under the influence of light, which then split into radicals leading to polymerization reactions. On purely theoretical considerations, Saha proposed following mechanism of degradation of lac:

$$\underset{\text{(lac)}}{\mathrm{RH}} + \mathrm{O_2} \xrightarrow{h\upsilon} \mathrm{R^{\cdot} + HOO^{\cdot}}\ \text{(slow)} \qquad \ldots\ldots\ (1)$$

$$\mathrm{R^{\cdot} + O_2} \longrightarrow \mathrm{ROO^{\cdot}} \qquad \ldots\ldots\ (2)$$

$$\mathrm{RO_2^{\cdot} + R-H} \longrightarrow \mathrm{ROOH + R^{\cdot}} \qquad \ldots\ldots\ (3)$$

$$\mathrm{ROOH} \longrightarrow \mathrm{RO^{*},\ RO_2^{\cdot},\ HO^{\cdot}} \qquad \ldots\ldots.\ (4)$$

$$\mathrm{RH + R^{\cdot}} \longrightarrow \mathrm{R-R^{\cdot}H} \qquad \ldots\ldots.\ (5)$$

$$\mathrm{HOO^{\cdot} + HOO^{\cdot}} \longrightarrow \mathrm{O_2 + H_2O_2} \qquad \ldots\ldots.\ (6)$$

$$\mathrm{2H_2O_2} \longrightarrow \mathrm{O_2 + 2H_2} \qquad \ldots\ldots.\ (7)$$

$$\mathrm{ROOH} \longrightarrow \text{Stable products} \qquad \ldots\ldots.\ (8)$$

Formation of hydroperoxides has been reported in a German Patent (Schmalz and Hoffman, 1963), by Sahu and Misra (1968) and also by Mukherjee and Sanyal (1971). The fact that no change in acid and iodine values was noticed for stored lac, suggests validity of reactions (1) to (3). It was suggested that involvement of hydroxyl groups in polymerization of lac on aging lead to inter-etherification, which also corroborates with observation of Palit. The rapid fall in flow and heat polymerization time during 6 month of storage may be attributed to above factor. McCullock (1943) reported infusibility of shellac after 175 days when kept over 75% relative humidity. The effect of water on shellac at room temperatures is to hasten gelation. Rapid decrease in flow and heat polymerisation time and also increase in hot alcohol insoluble suggest cross-linking or hydrogen bonding as the only mechanism of degradation of lac at high relative humidity.

Thermal polymerization of lac

When heated, shellac first softens and then melts. The molten mass gradually becomes thicker and on further heating, turns into a rubbery product, which on cooling solidifies to a hard, tough and horny mass. The original properties of lac change rapidly and final product becomes insoluble in alcohol, infusible, hard and brittle. The process is called hardening or curing and degraded product is termed as cured product. The time required to reach the rubbery stage was termed as life under heat or heat polymerization time heat polymerisation time by Ranganathan and Aldis (1933), which is similar to other thermosetting resins. The three stages were A, B and C respectively named by Gardner and Gross (1935). Shellac, which is soluble and fusible is considered to be in 'A' stage; the rubbery stage in which shellac is completely soluble in alcohol is 'B' stage and cured product is the final stage 'C' (Verman and Bhattacharya, *op. cit.* Bose *et al.*, 1963, and Gibson, 1938). The shellac remains mostly soluble when heated for specific time at a temperature less than heat polymerisation time. The alcohol insolubility increases very rapidly till 70% insolubility is reached; then rate slows down.

When shellac is heated above its melting point (120°–135°C), about 70% becomes insoluble and then the speed of the reaction slows down. If shellac is completely polymerized, 5°–10% of its constituents remain soluble in alcohol. This observation showed that shellac is not a fully thermosetting resin. This is corroborated with the observation that moulded discs prepared from shellac-urea-formaldehyde and shellac-melamine-formaldehyde can be powdered and reused for moulding. DSC thermograms (Fig.5.7) of heat polymerized seedlac and shellac revealed peak of resin (unpolymerised). Peak due to wax was not prominent due to its degradation owing to heating.

Degradation reaction, at elevated temperatures, is accompanied by gradual splitting of water vapour along with gradual rise in alcohol insoluble. About 5.3% water was reported to evolve by heating shellac at 200° to 220°C for 2 hr. It was concluded that thermal polymerization takes place *via* a chemical change accompanied by elimination of water and that the reaction is inter-esterification which proceeds at a high speed followed by inter-etherification at a slow rate. Shellac, on heating, is converted into massive molecular aggregates and also splits off water to form a small amount of anhydride. The following reactions may occur during thermal polymerization of lac (Bose *et al.*, 1963):

a. two carboxyl groups reacting with each other form anhydrides
b. carboxyl group of one molecule reacting with hydroxyl groups of another forming esters (or lactides)
c. two hydroxyl groups reacting with each other to form ethers, and
d. a hydroxyl atom and a hydroxyl group held by two adjacent carbon atoms reacting to produce unsaturation giving rise to some active centers of polymerization.

Three dimensional spatial arrangement at B stage is complex, further heating do not increase the molecular weight through condensation, resulting into a more entangled compact structure at C stage. Evidence of transformation of lac molecule to a more compact stage due to heating even at A stage, has been obtained from dielectric study where a reduction in relaxation time and Cole-Cole parameter was noticed with an increase in temperature from 80° to 110°C for shellac (Goswami and Bhattacharya, 1979), its constituents hard and soft resins (Goswami, 1979a) and also for other natural resins *viz.*, mastic, dammar (Goswami, 1982) and Manila copal (Goswami, 1977). Recently, in an FT-IR study on thermal degradation of shellac, Sarkar and Shrivastava (2000) attributed hydroperoxide formation and inter-etherification type of reactions to be primary reactions during the degradation process.

Effect of pressure

If shellac is heated under pressure, rate of hardening is retarded as B-stage shellac is easily converted to A-stage. Heating under pressure in presence of water is a reversible process as below (Bose *et al.*, 1963h):

$$\text{A-stageshellac} \underset{\text{pressure}}{\overset{\text{heat}}{\rightleftarrows}} \text{B-stage shellac + water}$$

This reversible nature of the reaction also explains why shellac is not mouldable by heat and pressure like other thermo-hardening resins. Thermal polymerization experiments carried out at 125°C of shellac revealed that practically no change in different chemical constants like acid, saponification, iodine and thiocyanogen numbers. However, a little decrease in OH value was noticed in the beginning, it remained almost constant up to the polymerized product.

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6

Spectral properties of lac

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ULTRA-VIOLET-VISIBLE ABSORPTION SPECTRA

ABSORPTION spectra of dewaxed shellac of different colour indices (0.6 to 35) and also of bleached lac were first reported by Goswami *et al.*, 1981 in ultra-violet and visible range in ethyl alcohol (Fig.6.1).

Absorption peaks were obtained at 225, 425 and around 290 nm for all shellacs (except for bleached lac). A few additional absorption maxima were obtained for bleached lac (Goswami *et al.*, 1981), Fig.6.2. The absorption peak at 425 nm was, however, found absent in bleached lac. The value of absorbance at 425 nm was found to increase with increase in the colour index of shellac (increase in pigment content), for a particular concentration (Fig.6.3). The result suggested that the peak at 425 nm was due to erythrolaccin (Bose *et al.*, 1963) present in shellac. A relationship was obtained when absorbance at 425 nm was plotted against colour index of shellac solution at 0.1%:

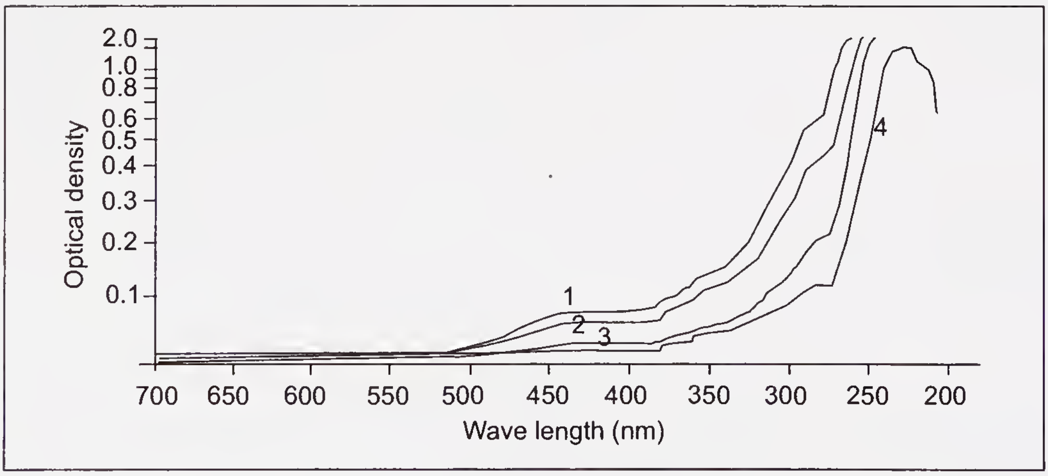

Fig. 6.1 Absorption spectra of dewaxed lemon shellac at different concentrations in the UV and visible range. (1) 1.5X 140^{-3}, (2)10^{-3}, (3) 4.5X10^{-4} and (4) 10^{-4} g/ml.

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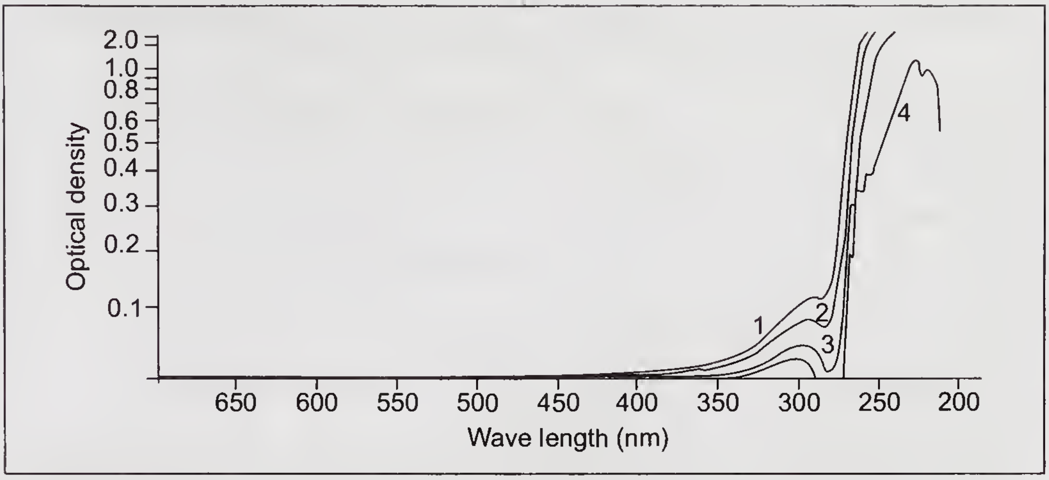

Fig 6.2 Absorption spectra of bleached lac at different concentrations in the UV and visible range. (1) $1.5X\ 10^{-3}$, (2)10^{-3}, (3) $4.5X10^{-4}$ and (4) 10^{-4} g/ml.

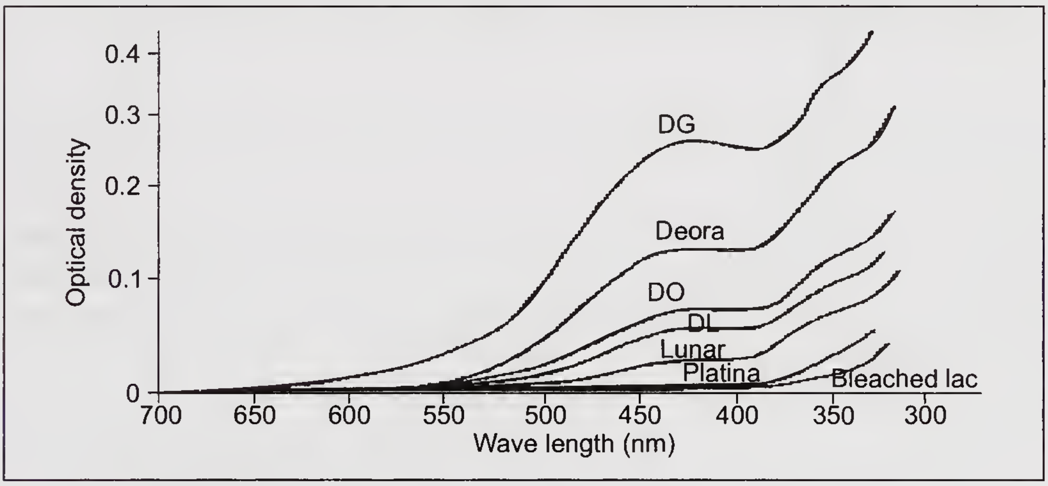

Fig. 6.3 Absorption spectra of different shellacs of various colour indices. Concentration for shellacs 10^{-3} g/ml.

$$\text{Colour index} = 136.9 \times \text{absorbance}$$

This relationship can be used for quick determination of colour index value of unknown sample of shellac by noting absorbance at 425 nm. The method was found easy and convenient compared to conventional method involving matching of colour of shellac solution with standard iodine solution. Later, this method was included as an alternative method of IS:6921-1973 (Amendment No.1) (IS:6921, Amd. 1989) and also in ISO (Shellac, Specification, Part 1 and 2, 1996).

At low concentration, absorption maxima were obtained at 225, 285 nm and a shoulder at 215 nm. Shoulder at 215 nm observed for dewaxed shellac was found replaced by a sharp peak in bleached lac. The peak at 225 nm (also other peaks, shoulder below 350 nm) was ascribed due to terpenic acids present in shellac (which possess unsaturation). Positions

Table 6.1. Position of absorption maximum for terpenic acids isolated from shellac and also from shellac and bleached lac*

Acids	Position of absorption maximum in nm
Shellolic	229
Epishellolic	228
Jalaric	210, 230, two small peaks at 260 and 275
Laccijalaric	222
Laksholic	228
Epilaksholic	225
Unidentified new acid	210, 225 and 274
Shellac (dewaxed)	225, shoulder at 350, 425(at concentration 10^{-4} g/ml) at 225, 285, shoulder at 215
Bleached lac	225, 290-300, small peaks at 255, 265

*Wadia and Khurana, 1969; Singh *et al.*, 1969; Prasad, 1979; and Goswami *et al.*, 1981.

of absorption maxima for different terpenic acids isolated from shellac in pure form. Table 6.1.

Goswami and Prasad (1982) studied absorption spectra of soft and hard fractions of shellac and also their different admixtures in ultra-violet and visible range. For soft lac, absorption maxima were noted at 225, around 290 and at 435 nm (Fig.6.4). For hard lac, absorption maxima were at 225, 255, 260, around 290 and at 425 nm (Fig.6.5). Interestingly, absorbance value at 225, 425 nm and $E^{1\%}{}_{1cm}$ value at 425 nm of 70:30 hard-soft lac mixture were found almost identical to those of shellac (Table 6.2), corroborating the proposition that shellac is a physical mixture of 70:30 hard-soft resin mixture (Fig.6.6).

Table 6.2 Absorbance characteristics of hard and soft lac resins and of their different admixtures*

Resins	Absorbance at 425 nm (Conc. 10^{-3} g/ml)	$E^{1\%}{}_{1cm}$	Absorbance at 225 nm (Conc. 10^{-4} g/ml)
Hard resin	0.04	0.5	1.7
Soft resin	0.076	0.8	0.91
Hard-soft resin mixture (70:30)	0.052	0.53	1,6
Hard-soft resin mixture (50:50)	0.062	0.63	0.62
Hard-soft resin mixture (20:80)	0.07	0.73	0.581
Shellac (DL)	0.057	0.54	1.65

* Goswami and Prasad, 1982.

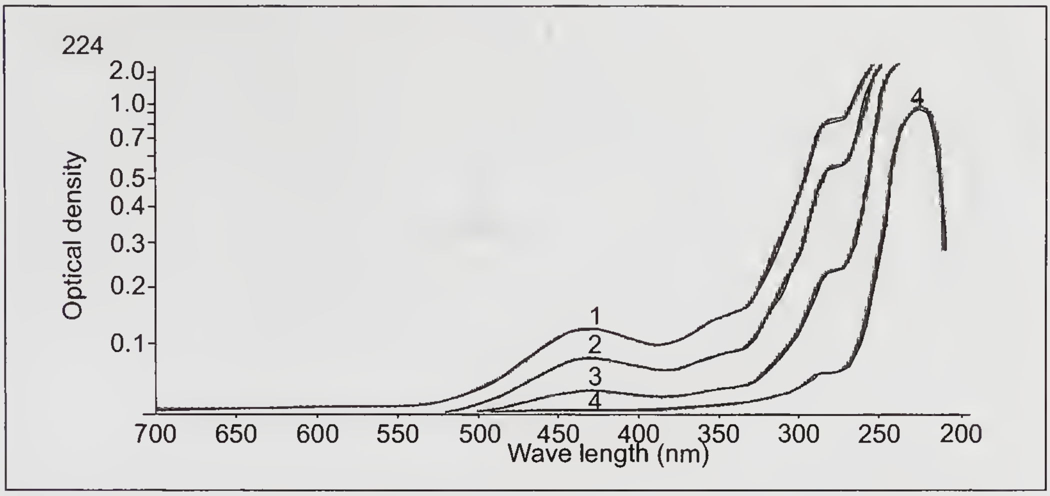

Fig. 6.4 Absorption spectra of soft lac resin at different concentrations in the UV and visible range.(1) 1.5 × 10^{-3}, (2)10^{-3}, (3) 4.5 × 10^{-4} and (4) 10^{-4} g/ml.

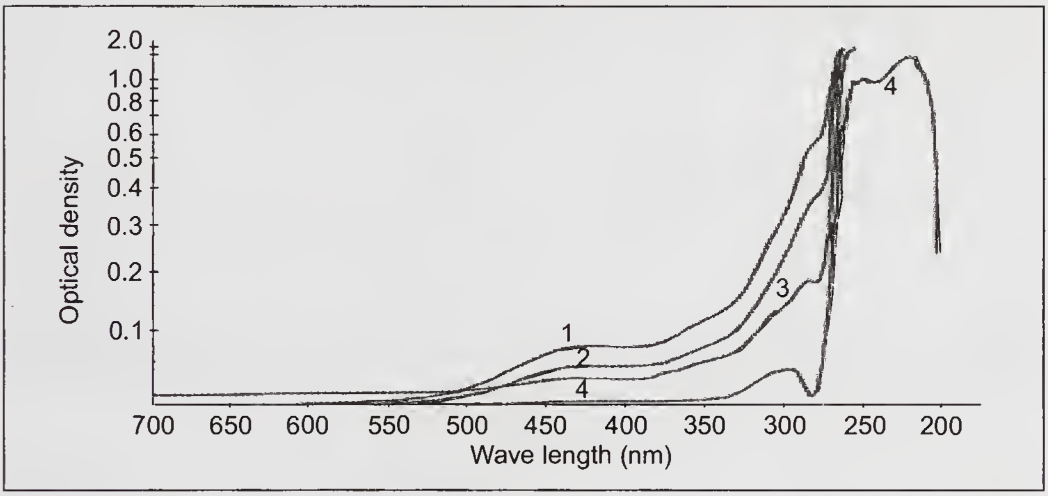

Fig. 6.5 Absorption spectra of hard lac resin at different concentrations in the UV and visible range.(1) 1.5X 10^{-3}, (2)10^{-3}, (3) 4.5X10^{-4} and (4) 10^{-4} g/ml.

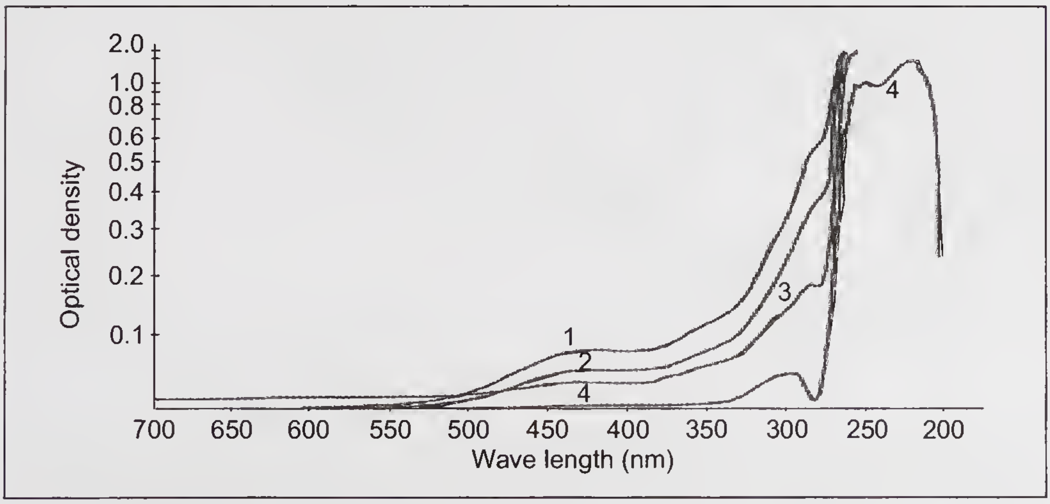

Fig. 6.6 Absorption spectra of 70:30. Mixture of hard and soft lac resin at different concentrations in the UV and visible range.(1) 1.5X 10^{-3}, (2)10^{-3}, (3) 4.5X10^{-4} and (4) 10^{-4} g/ml.

The higher absorbance noted for soft lac at 425 nm was attributed to presence of more erythrolaccin compared to that present in hard fraction, which is also evident from physical appearance of two fractions. The spatial distribution of the different polar groups present in the 70:30 admixture is not identical to that present in parent shellac (Goswami and Prasad, 1982).

Agarwal *et al.*(1993) investigated absorption spectra of resins recovered from different by-products obtained during processing of lac (from two strains *kusmi* and *rangeeni*) in ultraviolet and visible range at two different concentrations including those of seedlac and shellac (Figs.6.7 and 6.8) in

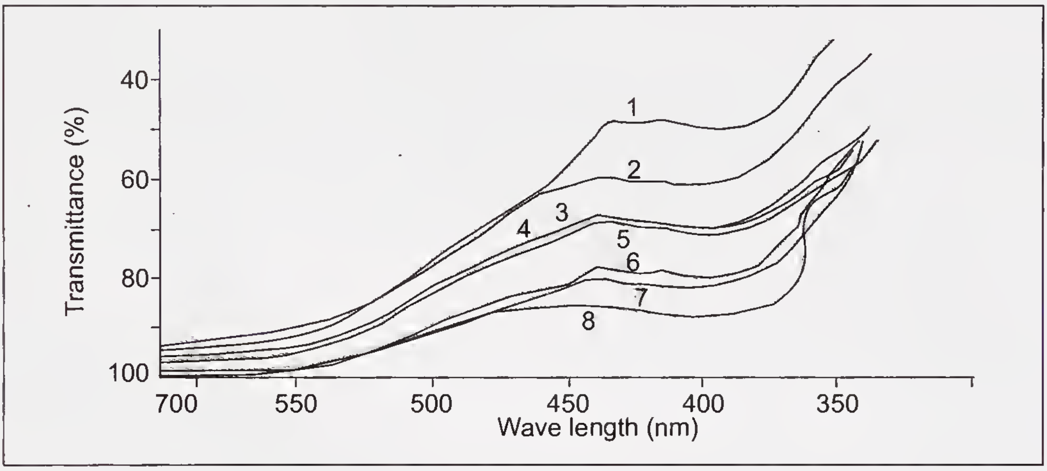

Fig. 6.7 Absorption spectra in the visible range of seedlac, shellac and of resins recovered from different byproducts obtained from the *kusmi* strain. (1) *Ghongi*, (2) *Patti*, (3) *Molamma* (after soda wash), (4) *Molamma* (before soda wash), (5) *Kunhi*, (6) Seedlac, (7) *Kiri*, (8) Shellac. Concentration 10^{-3} g/ml.

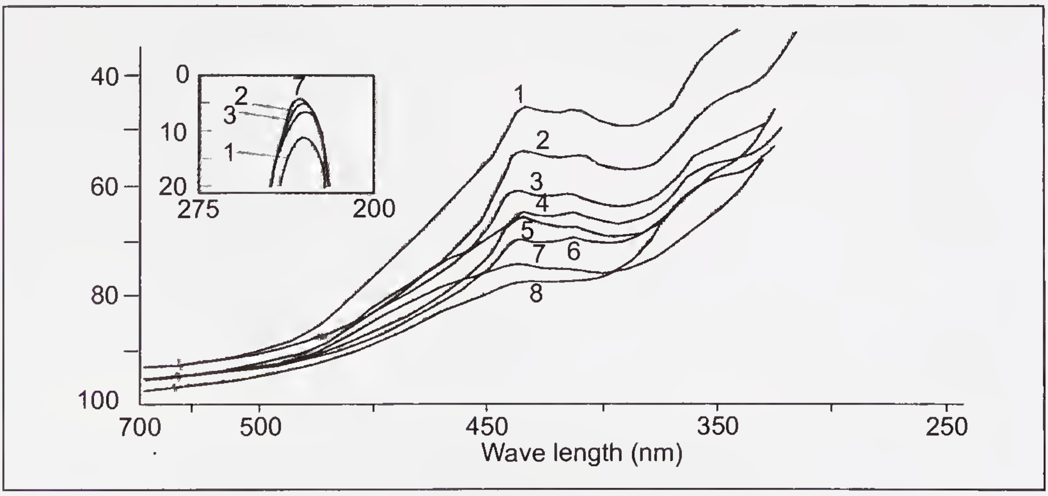

Fig. 6.8 Absorption spectra in the visible range of seedlac, shellac and of resins recovered from different byproducts obtained from the *rangeeni* strain. (1) *Molamma* (before soda wash), (2) *Molamma* (after soda wash), (3) *Ghonghi*, (4) *Kiri*, (5) *Kunhi*, (6) Seedlac, (7) *Patti*, (8) Shellac, concentration 10^{-3}g/ml. Inset: absorption spectra in the range 200–275 nm (concentration 10^{-4}g/ml)

absolute alcohol. The absorption spectra of recovered resins and of seedlac and shellac provided information regarding relative presence of dyes and other chromophoric groups. The recovered resins from the *rangeeni* strain exhibited absorption maxima at 235, 412.5 and 435 nm and a shoulder at 350 nm. The maximum noticed at 412.5 nm for resin recovered from *kunhi* was not so prominent, but for shellac absorption maximum was noticed at 425-30 nm. Two absorption maxima were noticed at 417.5 and 437.5 nm for resin recovered from *ghongi*, *kunhi* and seedlac of *kusmi* strain. The resins recovered from *molamma* (both before and after soda washing), *patti* and *kiri* exhibited only one maximum at 440 nm, but for shellac maximum occurred at 425-30 nm. The absorption maximum noticed around 425-30 nm for seedlac, shellac and for resins recovered from byproducts was attributed due to erythrolaccin present in the resins. The additional peaks around 412.5 to 417.5 in seedlac and resins recovered from different byproducts were probably due to laccaic acid present in resins along with erythrolaccin which could not be removed during washing with water (Agarwal *et al.*,1993).

Absorbance at 425 nm provided information regarding dye content present in resins recovered from byproducts (Table 6.3). Since, *ghongi* is obtained first and *kiri* is the last byproduct during processing of lac, gradual lowering in absorbance indicated gradual reduction in dye content due to progressive processing. The little higher value of absorbance observed at 425 nm for resin recovered from *kiri* compared with shellac was due to the darkening of the resin due to heat treatment.

Goswami and Prasad (1988) investigated absorption spectra of natural resins, kauri, pontianac, benzoin, gamboges, dragon and also different admixtures with shellac in ultra-violet and visible range in ethyl alcohol.

Table 6.3. Absorbance noted at 425 nm of the resins recovered from seedlac, shellac and resins recovered during processing of lac*

Sample	Absorbance at 425 nm	
	Kusmi	*Rangeeni*
Ghonghi	0.27	0.33
Patti	0.24	0.30
Molamma (before soda washing)	0.18	0.22
Molamma (after soda washing)	0.16	0.18
Kunhi	0.13	0.13
Seedlac	0.10	0.15
Kiri	0.09	0.118
Shellac	0.06	0.11

* Agarwal *et al.*, 1993.

Table 6.4. Positions of absorption maxima and shoulder of different natural resins*

Natural resins	Position of absorption maximum (nm)	Position of shoulder (nm)
Kauri	230,265, 275	-
Pontianac	240, 280	310
Benzoin	232.5, 280	-
Rosin	225, 245	300
Gamboge	220, 240, 485	290
Dragon	235, 285, 475	350
Shellac	225, 290, 425	215, 350

* Goswami and Prasad, 1988.

All above natural resins exhibited distinct absorption maxima in ultraviolet range (Table 6.4). Gamboge and dragon exhibited absorption maxima in visible range also (Goswami and Prasad, 1988). These resins were found to contain water-soluble dyes. Identification of shellac in the presence of the above natural resins was possible by the inspection of absorption spectra (presence of maximum at 425 nm, characteristic of shellac) of admixtures when the concentration of shellac was at least 10-fold that of the other resins in admixture (Goswami and Prasad, 1988).

Infra-red spectra

Stair and Coblentz (1935) studied IR spectrum of lac, in which presence of =CH-, $-CH_2-$ and $-CH_3$ as well as C=O groups was identified. Edwards *et al.* (1996) reported FT Raman vibrational modes of resin from lac samples obtained from museum and archeological artifacts. Sarkar and Shrivastava (1997) studied FTIR spectroscopy of MM shellac, Fig. 6.9, which revealed peaks at 3438 cm^{-1} (intermolecularly H-bonded hydroxyls), and at 2925 and 2853 cm^{-1}, attributed to C-H stretch of aliphatic $-CH_2-$ and $-CH_3$ and at 1718 cm^{-1} due to C=O stretch of –COOH overlapped with C=O stretch of α, ß-unsaturated ester. A shoulder of the stronger C=O peak has been reported at 1636 cm^{-1} for ethenoid C=C stretch; O-H bend and C-O stretch of aliphatic carboxyl and hydroxyl groups at 1252 cm^{-1} and 1158 cm^{-1} due to overlapping with C-O stretch of –COOR. The band at 1032 cm^{-1} is indicative of presence of C-O stretch of ether/ acetal linkage.

The band at 937 cm^{-1} was attributed to rocking vibration of the $C-CH_3$ superimposed with C-H wag of the disubstituted *trans* olefin (Sarkar and Shrivastava, 1997). A sharp peak at 721/cm is evidence of C-H bending (out of plane) of *cis* alkene. There is a distinct possibility of mechanical coupling among adjacent C-O, C-C stretch and O-H and $-CH_3$ bending modes, as close lying vibrational levels having similar symmetry properties were allowed to mix so closely that each can take on some of the character of the other (*cf.* Fermi resonance).

The bands between 1000/cm and 1350/cm cannot be described in terms of simple motion of specific functional groups, but only in terms of probable assignments as stated earlier (Sarkar and Shrivastava, 1997).

Sarkar and Srivastava (1998) from FT-IR studies on bleaching of lac revealed that no major changes in functional groups occur as envisaged by previous workers. Acid hydrolysis of acetal linkages instead of acid catalysed polymerization (thought earlier) was ascribed to the degradation of bleached lac (Sarkar and Srivastava, 1998). Studies on FT-IR (Sarkar and Srivastava, 2000) on thermal degradation of lac resin suggested that hydroperoxidation and inter-etherification are plausible reactions than inter-esterification and dehydration. Sarkar and Kumar (2001) reported that FT-IR spectra of different forms of lac resin *viz.*, stick-lac, seedlac and shellac. The degree of polyesterification between the component acids in freshly harvested stick-lac was found less than present in seedlac. No spectroscopically significant difference was observed between seedlac and shellac (Sarkar and Kumar, 2001). Interestingly, *rangeeni* lac was found to have higher unsaturation and hydroxylic content compared to *kusmi* lac (Sarkar and Kumar, 2001). Normal *kusmi* lac was reported to contain long chain of unsaturated fatty acids compared to mutant *kusmi* variety (Sarkar and Kumar, 2001). No such difference was observed in resin obtained from the *rangeeni* strains.

Pyrolysis silylation with GC-MS

Pyrolysis with hexamethyldisilazane is a useful procedure for GC-MS analysis of polar constituents characterizing different natural resins. Shellac produces a series of short chain fatty acids, when subjected to conventional pyrolysis (Chiavari *et al.*, 1995), a behaviour unique among resins. However, these products can also be produced by thermal breakdown of long chain fatty acids present in lipidic materials. Thus, it may be difficult to detect presence of shellac in a mixture of resin and oil or egg by conventional pyrolysis.

Pyrolysis-silylation (silylating agent – Hexamethyldisilazane, HMDS) in combination with GC-MS was applied for analysis of natural resin, shellac. Pyrolysis with HMDS confirmed presence of fatty acids in silylated esters, but, in addition, gave rise to production of other characteristic compounds (Table 6.5). The mass spectrum of most intense peak revealed presence of base peak (73 m/z ion). It showed that compound contains at least a trimethylsilyl (TMS) group. The ions at m/z 385 and 327 might have resulted from the loss of a methyl and TMS from 400 amu, suggesting that ion m/z 401 is the protonated molecular ion (Chiavari *et al.*, 2002).

Table 6.5. Products arising from pyrolysis silylation of shellac*.

Peak no.	Fragments	Molecular weight	Main ions in Mass spectrum (m/z)
1	Pentanoic acid TMS ester	174	75, 159, 117
2	Hexanoic acid TMS ester	188	75, 173, 117
3	Heptanoic acid TMS ester	202	75, 117, 187
4	Octanoic acid TMS ester	216	75, 117, 173
5	Benzoic acid 3 methyl TMS ester	208	119, 191, 193, 208
6	Propanoic acid 3 phenyl TMS ester	222	133, 163, 207, 222
7	2 Propenoic acid 3 phenyl TMS ester	220	131, 205, 161, 220
8	Dodecanoic acid TMS ester	272	73, 117, 257
9	Tetradecanoic acid TMS ester	300	73, 117, 285
10	Palmitic acid TMS ester	328	73, 117, 313
11	Silylated compound		73, 274, 303, 327
12	Silylated compound		73, 93, 129, 217, 243
13	Silylated compound		73, 93, 150, 217

* Chiavari *et al.* 2002.

Presence of benzenic compounds indicated that they probably could be derived from rearrangement of sesquiterpenic alicyclic compounds (Chiavari *et al.*, 2002).

Luminescence spectroscopy

The technique is used to study spatial distribution of materials and molecular changes that occur as the function of time. Larson *et al.*(1991) investigated luminescence spectra of various natural resin samples, including dammar, mastic and sandarac (tree resins), copal (fossil resin), shellac (insect derived) and rosin (resin from balsam distillation).

Of various resins studied, dragon's blood and shellac could be easily differentiated from others. The emission observed using ultraviolet excitation from each of these samples was further to red, showed peaks between 15,000 and 18,000/cm, than emission observed from other resins studied. They exhibited emission maxima clearly different from those observed with other resins, which emitted farther to blue. Besides luminescing further to red, both bulk and film samples of dragon's blood and shellac showed structure in their spectra.

Larson *et al.* (1991) studied effects of sample origin and/or aging of shellac in bulk and film cast from its solution in ethyl alcohol. Both the bulk and film samples exhibited emission peaks or shoulders at 16,500, 15,800, and 14,700 cm^{-1}, but relative intensities of these were different between bulk and film spectra. The aged film showed only two features in its emission spectrum; a peak at 17,000 cm^{-1} and a shoulder at 16,000

cm^{-1}. The emission spectrum of aged orange shellac film is shifted to slightly higher energies with respect to newer sample.

Raman spectroscopy

It is a non-destructive spectroscopic method, which is used for identification of small samples (typically less than 1 μg) of material used in objects of art such as inorganic and organic pigments, natural binders and varnishes. Raman-spectra are fingerprints of molecular structures of these materials, which are used for their identification and for study of degradation processes.

Raman spectra of four natural resins shellac, dammar, colophony and copal were investigated by Vandenbeele *et al.*(2000). These are mainly applied as varnish, consist of a complex mixture of alcohols, carboxylic acids, ketones, polycyclic hydrocarbons and aromates. These materials all contain mainly terpenoid components with multiple C=C double bonds. A characteristic Raman band of these components is the ν (C=C) stretching band of *cis* alkenes (~1650 cm^{-1}). A weak band at *ca.* 1240 cm^{-1} is attributed to in plane C-H bending of *cis* alkenes. The broad band at *ca.* 1450 cm^{-1} is assigned to δ (CH_2) scissoring mode. As resins consist of complex mixtures of terpenoid materials, their spectra depend on this composition and it is possible to discriminate between different types. Resinous materials (like shellac, dammar, colophony and copal) are characterized by distinct C=C bands in their spectrum.

Spectrophotometric studies on lac dye

Laccaic acid is one of the minor constituents of stick-lac and is present to the extent of nearly 1%. The pinkish solution obtained, at the washing of stick-lac with water for conversion into seedlac, is due to this water-soluble dye.

Table 6.6. Absorption peaks of laccaic acid in different solvent systems*

Solution of laccaic acid prepared in different solvents	Concentration of Soln (%)	Absorption maxima (nm)
Water	0.001, 0.002, 0.003, 0.004 and 0.005	292 and 490
Ethanol	0.001, 0.002, 0.003, 0.004 and 0.005	230, 292, 340, 500 and 530
Methanol	0.001, 0.002, 0.003, 0.004 and 0.005	230, 292, 340, 500 and 530
Acetone	0.001, 0.002, 0.003, 0.004 and 0.005	500
Sodium salt of laccaic acid in water	0.001, 0.002, 0.003, 0.004 and 0.005	530

*Prasad *et al.* (1984)

Prasad *et al.* (1984) studied the absorption spectra of laccaic acid in different solvents in the UV-visible range. Solutions of pure laccaic acid in water, ethanol, methanol and acetone (0.001, 0.002, 0.003, 0.004 and 0.005% in each case) were prepared and absorption peaks of UV-visible absorption spectra recorded (Table 6.6).

Dye solution in ethanol or methanol gave five absorption peaks at 230, 292, 340, 500 and 530 nm, whereas in water it gave only 2 absorption peaks, at 292 and 490 nm respectively. In acetone, only one absorption peak was observed at 500 nm. Sodium salt of laccaic acid dissolved in water gave one absorption peak at 530 nm. The shift in position of absorption peak may occur with polar compounds, if different solvents are used. It is obvious from the Table 6.6 that the absorption peaks of laccaic acid in ethanol or methanol for all concentrations are at the same wave lengths, whereas in water a shift of nearly 10 nm (on lower side) takes place in the visible region.

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Electrical Properties of Lac

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DIELECTRIC MATERIALS are indispensable in electrical engineering. These are used to cover current conducting parts of electrical devices and to isolate parts maintained at different potentials. Depending on the different applications, dielectric materials are to satisfy certain requirements, in regard to mechanical, heat resistance, physico-chemical properties of materials and also ability of materials to withstand certain treatments. Thus, for a particular use, the materials are chosen which satisfy a desired combination of properties.

Shellac, widely known for its good insulation properties, is the oldest natural resin. Use of shellac in hot-melt electrical insulating coating for telegraph insulators was reported in 1852. Since, use of an insulator requires knowledge of different parameters, dielectric constant, dielectric loss, dissipation factor (Tan δ), dielectric strength and also their variations under different temperature, frequency, humidity conditions for different engineering applications, studies have been made by various researchers.

Dielectric behaviour of shellac

Value of dielectric constant of an insulating material is important in determining capacitance of condenser in which material is used as a dielectric medium. The dielectric constant of shellac is stated to vary between 2.7 and 3.7 (Table 7.1) in the International Critical Tables (Verman, 1936).

Table 7.1. Value of dielectric constant of shellac.

Dielectric constant of shellac at infinite frequency	Author	Year
2.95–2.73	Wuellner	1887
3.1	Winklemann	1889
3.67	Donle	-

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[1] Ex-Principal Scientist.

Table 7.2. Variation of dielectric constant of shellac due to immersion in water.

Condition of test	Dielectric constant
Initial (before immersion)	3.62 – 3.71
After six month immersion	7.7 to 20
After drying	3.58

Lee and Lowry (1927) studied variations of dielectric constant of shellac resulted due to immersion in water (Table 7.2). Water of absorption was reported to vary from 4.3 to 5.1%. Shellac was found to regain its dielectric constant value after drying (Table 7.2); 3.6 may be taken as the value of dielectric constant of shellac at room temperature.

Bhattacharya (1944) made a detailed study on the dielectric behaviour of shellac in frequency range 50 Hz to 500 kHz and at temperatures between 20° and 110°C (Fig.7.1). A little decrease in dielectric constant was observed with frequency at temperatures 20° to 40°C. Appreciable dielectric dispersion was found for temperatures higher than 40°C.

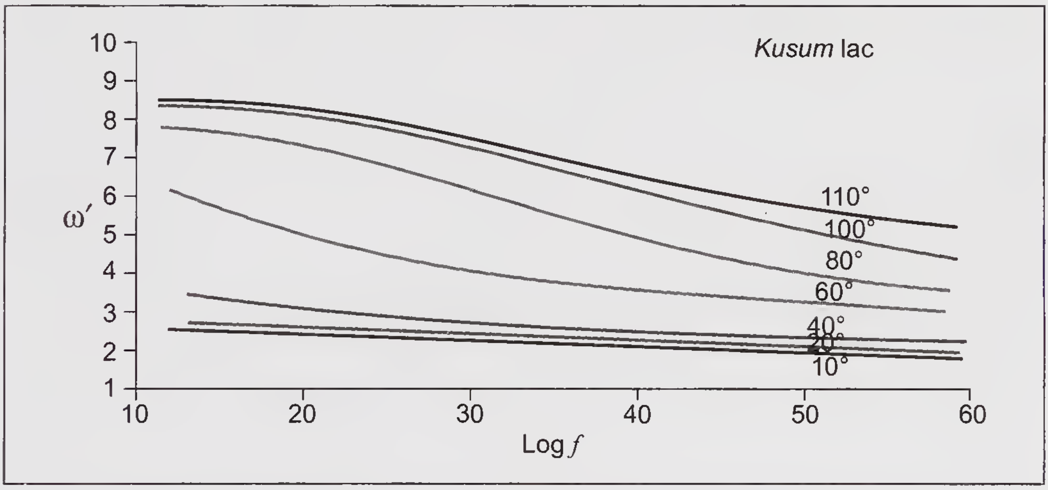

Fig. 7.1 Dielectric dispersion curves of shellac at different temperatures

Dielectric loss

It is the power dissipated in a dielectric as heat when subjected to an electric field. It depends on the molecular structure and type of molecule. If molecules (free from impurity) are non-polar, dielectric loss is negligible. Polar molecules exhibit high loss values. An idea about value of dielectric loss/Tan δ and its nature of variation with frequency and temperature is essential not only for manufacturing condensers but also in designing insulators where it is required to avoid power loss. The variation of dielectric loss and Tan δ with temperature and frequency of shellac was studied by Bhattacharya (1944). The values noticed at 50 Hz and at 20°C were 0.015 and 0.004. Plots of dielectric loss/Tan δ with temperatures at different frequencies revealed a shift in peak towards higher frequencies.

This indicated conformational change/rearrangement in lac molecules with rise in temperature. The dielectric behaviour of shellac was attributed to the rotation of the hydroxyl groups in the alternating field (Bhattacharya, 1944). At low temperature, the polar groups find hindrance for orientation in response to alternating field giving a low value of dielectric loss/Tan δ. The orientation is more favoured with softening of resin with increase in temperature, yielding an increase in the parameters.

Many relaxation processes

Dielectric relaxation data obtained by Bhattacharya (1944) were analysed by Cole-Cole (1941) method by Goswami (1979) for obtaining information regarding relaxation processes and conformational changes undergone by resin molecules during thermal transition from solid to liquid state. The Cole-Cole patterns of shellac revealed 3 relaxation processes for temperatures 20° to 60°C (marked a, b and c in Fig.7.2), two relaxation processes at 70°C and one at 80°C and above. Processes a and b were attributed to arise from orientation of segments. Process c was interpreted to arise from relaxation of a polar group, probably the OH groups; it became insignificant with rise in temperature when decrease in viscosity favoured orientation of larger segments (Goswami, 1979). The patterns at 80°C and above were interpreted to arise from molecular motions (Goswami, 1979). Many relaxation processes are generally observed in polymers, thus indicating shellac is a polymeric material. Goswami and Walker (1993) studied dielectric properties of air-dried films of shellac, prepared from its solution in C_2H_5OH, ethyl alcohol, at different frequencies between 20 Hz and 100 kHz and at temperatures 20° to 120°C. The conductance vs. temperature plots at different frequencies also revealed three relaxation processes. This provided experimental evidence of multi-relaxation processes observed in Cole-Cole diagrams. Variation of static dielectric constant (ε_0) with temperature (Fig.7.3) indicated three distinct phases during thermal transition from solid to liquid state (Goswami, 1979). Plot capacitance vs temperature (Fig.7.4) also revealed similar phenomenon (Goswami and Walker, 1993). T_g and T_m values were found around 40° and 70°C respectively from both $\in_0$/capacitance vs temperature plots. Goswami (1979) reported a decrease in relaxation time and Cole-Cole parameter of shellac above 80°C indicating that molecules became more compact due to cross-linking (Goswami, 1979). Cole-Cole patterns obtained were similar to those of other natural resins like, Manila copal (Goswami and Bhattacharya, 1977), mastic, dammar (Goswami, 1982), shellac-urea-formaldehyde (Goswami, 1985) and shellac-melamine-formaldehyde (Goswami, 1985) moulded discs.

Shellac is known to form cross-linkages when heated at and above 150°C and it becomes infusible. Dielectric studies were also made on shellac films baked at 200°C by Goswami and Walker (1993). The conductance

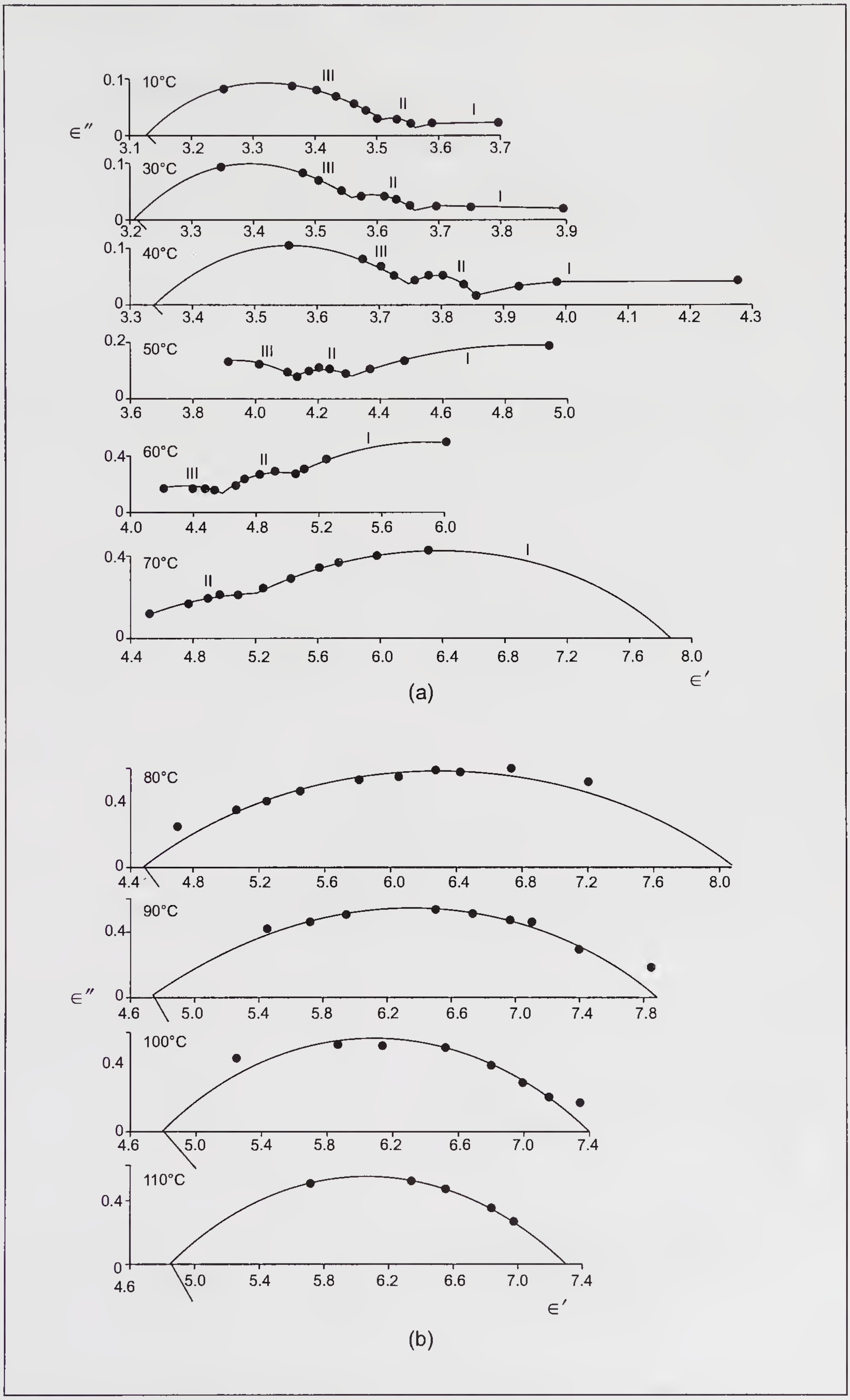

Fig. 7.2 Cole-cole plots of shellac at different temperatures

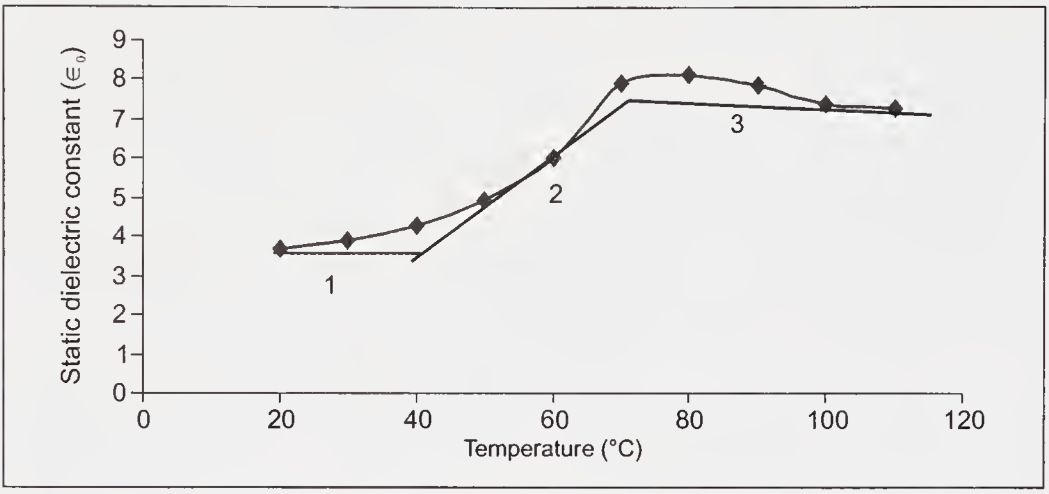

Fig. 7.3 Variation of static dielectric constant with temperature of shellac [solid to liquid, three phases, are indicated as 1,2,3]

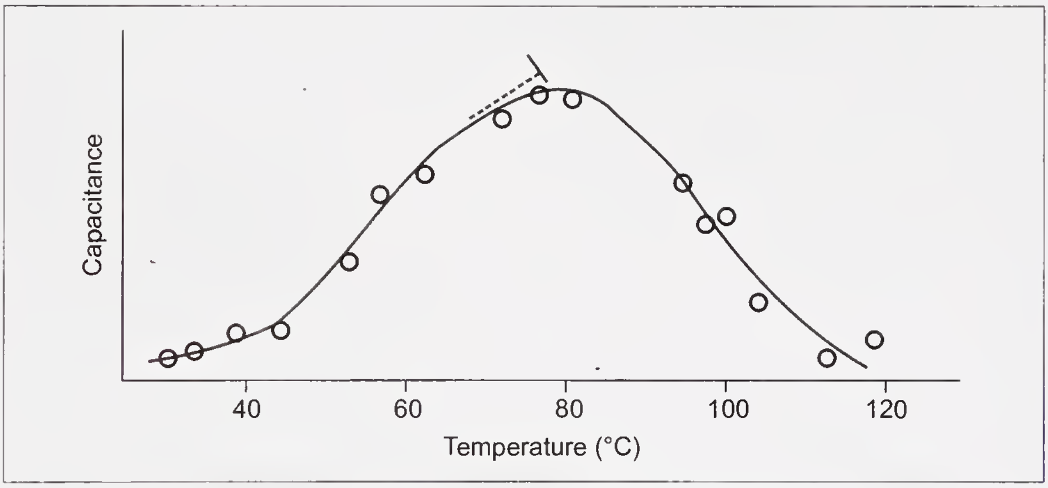

Fig. 7.4 Variation of capacitance with temperature of shellac film cast from solution in ethyl alcohol

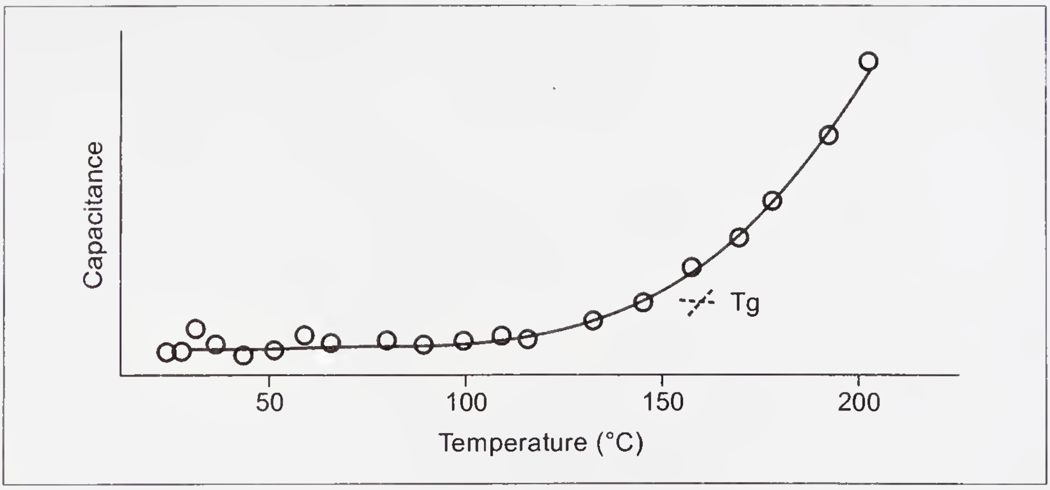

Fig. 7.5 Capacitance versus temperature plot of baked films of shellac. T_g is around 120°C compared to 40°C for air dried shellac films

vs temperature plots at different frequencies indicated almost constant value up to about 150°C for frequencies 12 and 25 Hz. The major conductance peak, observed at 80°C for air-dried films, was found to occur at a higher temperature with increase in frequency. The capacitance vs temperature plots of baked films at 12-100 Hz (Fig.7.5), were found different compared to those for air-dried films (Fig.7.4) and $\in_0$ vs temperature plot (Fig.7.3) of normal shellac. Capacitance values were found to remain almost constant up to 120°C; the glass-transition temperature was noticed around 140°C (Fig. 7.5). Almost constant values of conductance and capacitance up to a relatively higher temperature and the rise in Tg from 40° to 140°C for baked shellac films confirmed cross-linking of shellac molecules due to heating, which caused hindrance for segmental orientation (Goswami and Walker, 1993). The rise in capacitance value beyond 140°C, for the baked films, suggested that shellac does not become fully thermosetting, even heating at 200°C (much above heat polymerization time).

Surface and volume resistivities

Knowledge of above parameters is essential, as these determine effective resistance of an insulating material. Dietrich (1910) studied effect of light, moisture and temperature on the electrical resistivities of various insulating materials including lac. No detectable change in resistivity of lac was observed on its exposure to light up to 47 days. No conclusive results were obtained on the effect of moisture. The value of resistivity decreased from a value 10^{14} to 10^{15} Ohm cm at 20°C to a value of 10^{11} for a rise of temperature up to 80°C. Staeger (1931) obtained a higher value on prolonged heating at elevated temperature. A higher value was also reported for hard resin than shellac.

Table 7.3. Variation of volume resistivity with temperature of shellac and a few moulded compositions.

Materials	Temperature (°C)	Volume resistivity × 10^{13} Ohm cm
Kusum shellac	28.4	262
	38.0	54.1
	42.6	28
	50.0	9.8
Shellac powder SUF 91	30	139
	40	95.7
	50	62.1
	60	28.9
	70	7.6
	80	1.4
Shellac powder SAF 20	27	42.2
	40	35.2
	50	21.4
	60	14.3
	70	5.1
	80	1.2

Curtis (1914) found value of surface resistivity of sealing wax (cast) higher than shellac. Molten shellac was found to possess a value 1000-fold than that obtained for films prepared from alcoholic solution. The low value for films was ascribed to solvent retained in

Table 7.4. Variation of volume resistivity with humidity of a few shellac compositions.

Materials	Volume resistivity × 10^{13} Ohm cm at relative humidity			
	0	30	60	90
Kusmi shellac	262	159	135	80
SUF 91	103	66	12.7	8.2
SMF 49	80	11	5.1	3.1
SUF 244	167	15.2	6.8	2.4
SUF 72	64	42	3.6	1.8
SUF 23	96	25	1.6	0.73
SAF 20	40	26	4.4	2.1
SC 93	16	7.6	1.3	0.51

SUF; Shellac, Urea and Formaldehyde; SMF; Shellac, Melamine and Formaldehyde; SAF: Shellac, Alcohol and Formaldehyde; and SC: Shellac

Table 7.5. Variation of surface resistivity with humidity of a few shellac compositions

Materials	Surface resistivity × 10^{13} Ohm cm at relative humidity			
	0	30	60	90
Kusmi shellac	760	660	180	73
SUF 91	590	320	100	20
SMF 49	380	160	14	2.5
SUF 244	480	190	24	16
SUF 72	295	216	33	3.6
SUF 23	200	140	19.6	4.2
SAF 20	830	380	7.6	4.9
SC 93	175	113	10	0.42

SUF; Shellac, Urea and Formaldehyde; SMF; Shellac, Melamine and Formaldehyde; SAF: Shellac, Alcohol and Formaldehyde, SC: Shellac

film. Bhattacharya (1942) made a detailed study on the volume and surface resistivities of lac and a few more moulded compositions based on shellac, urea, formaldehyde (SUF) and shellac, melamine, formaldehyde (SMF). A decrease in resistivities was noticed for an increase in temperature or humidity (Tables 7.3 to 7.5). The resistivities of SUF and SMF compositions were low when compared to those of shellac. From a comparison of the resistivities of plastic materials, it was found that shellac-based compositions may be classed among those which possess high resistivities.

Conduction in shellac

Gupta and Prasad (1979) studied conductivity of dewaxed decolourized (platina) shellac as a function of applied electric field and temperature. Different conduction mechanisms were operative for different stages of electric field and temperature as reported from plot of current density (J) vs. electric field (F). The ln J vs. ln F plot revealed that at low electric fields (up to 1200 v/cm) the conductance was non-Ohmic between 0° and 30°C, following nearly $J \infty F^{1/2}$ law. At 46°C, it was found to be first Ohmic and then changed to $F^{1/2}$ law. Purely Ohmic conduction was observed at higher temperatures. From $\ln J_m$ to $F^{1/2}$ and $\ln (J_m - J_o)$ vs. $F^{1/2}$ plots (where J_m, measured value of current density and J, extrapolated value of Ohmic current density), as reported, Schottky and 3-dimensional Poole-Frenkel processes were operative at high electric fields (above 2500 v/cm) and the current was space charge limited at intermediate electric field (1200 to 2500 v/cm). From Richardson's plot, the value of work function was found 0.775 eV.

Dielectric strength

As surface and volume resistivities of an insulator determine its behaviour under actual working conditions, dielectric strength also determines its efficiency in case of accidental over voltage. A dielectric in an electric field may lose its insulating property, if applied electric field strength exceeds a certain critical value (which is specific for a dielectric material). This is called dielectric breakdown. The voltage, at which a dielectric material punctures, is called breakdown voltage and field strength is called dielectric strength/breakdown strength/electric strength (Table 7.6).

Table 7.6. Dielectric strength of shellac

Materials	Value (kV/mm)	Author
Orange shellac	20-40	Fleming and Steel
Garnet shellac	14-18	Fleming and Steel
Shellac varnish film	36-48	Fleming and Steel
Shellac from solid casting	40	Poole
Shellac from alcoholic solution	25	Poole
Varnish film (AC)	80 (AC)	Mackay
Varnish film (AC)	200 (DC)	
Shellac	17-21	Warren
Moulded composition	40-160	Gardner and Whipple

Staeger reported that repeated melting of shellac resulted in decrease in dielectric strength. This was ascribed to formation of water due to condensation reaction. This was stated to be contradictory, because such water, if any, was expected to reduce resistivity; but in practice, Staeger (1931) observed an increase in resistivity.

Table 7.7. Dielectric strength of shellac at different temperatures

Materials	Temperature (°C)	Dielectric strength (kV/cm)
Shellac	20	24.4
	30	6.4
	At melting point	4.7
	In molten state	4.2

Bhattacharya (1942) studied the variation of dielectric strength with thickness of moulded discs prepared from shellac and shellac-urea-formaldehyde wood flour composition. A decrease in dielectric strength was observed with an increase in thickness of material. For most of the insulating materials, variation in the breakdown voltage (V) is related with thickness (t) of the specimen by the equation: $V = At^n$, where, A and n are constants, value of n being less than unity. For lac as well as Shellac-urea-formaldehyde (SUF) compositions, above formula is found to be applicable. Lakshminarayanan and Gupta (1979) later found that moulded discs prepared from shellac-butylated melamine formaldehyde and shellac-butylated urea formaldehyde resin blends obeyed above- mentioned law. Effect of surrounding medium on dielectric strength of the insulators was studied and it was found that specific resistance of medium was responsible for difference in dielectric strength. (Bhattacharya (1942) Table 7.8.

Table 7.8 Specific resistance and dielectric constant of the surrounding media

Surrounding medium	Specific resistance (Ohm)	Dielectric constant
Castor oil	2×10^{13}	4.58
Transformer oil	7×10^{12}	2.20
Kerosene oil	5×10^{11}	2.10
Xylol	6×10^{10}	2.36
Spt of turpentine	7×10^{8}	2.23
Xylol + 12% acetone	1×10^{8}	3.12

According to recent study dielectric strength of shellac can be taken as 40 kV/mm for all practical purposes. Freshly prepared shellac (from *palas, ranginee*) even yielded dielectric strength in the range of 40 to 80 kV/mm (Khanna *et al.,* 1986).

Effect of pressure on dielectric constant of shellac

Ackerlind and Weber (1938) made an extensive study on effect of pressure on the dielectric constant of shellac films (prepared from varnish) measured at 60 Hz and 1 K Hz. The film thickness for such studies recommended was 0.09 mm. For thicker films, an increase in

Table 7.9. Variation of dielectric constant of shellac with pressure (at 60 Hz, 300V)

Pressure (g/cm^2)	Dielectric constant
0	3.23
21	3.30
28	3.33
64	3.39
119	3.45
64	3.44
28	3.39
21	3.39
0	3.37

dielectric constant was observed with increase in applied voltage. The voltage effect was ascribed to residual alcohol in the films. The dielectric constant values of a film at 60 Hz and 1 kHz were found to approach same value with increase at the drying. Effect of pressure on dielectric constant was also studied. A little decrease in dielectric constant was observed with increase in pressure, the value attained almost original value on withdrawal of pressure (Table 7.9).

Effect of storage on dielectric parameters

The data available on the subject are meagre. Khanna *et al.* (1986) studied effect of storage on different physico-chemical properties of seedlac and shellac. The electrical properties were dissipation factor, conductivity (both 5% w/v solution in alcohol measured at 100 kHz) and dielectric strength of varnish. For all above parameters, an initial rapid decrease was observed with time, after which decrease was not appreciable and a plateau was reached. The decrease in dissipation factor was attributed to decrease in OH groups available for relaxation. The decrease in dielectric strength indicated deterioration in insulation strength of resin due to aging. The low value of dielectric strength of seedlac when compared with shellac was owing to impurities present in the former. This explains also higher values of both dissipation factor and conductivity observed for seedlac samples compared to those of shellac.

Dielectric behaviour of constituents of shellac

Bhattacharya (1944) studied dielectric behaviour of chief constituents of shellac, soft and hard fractions in frequency range 50 Hz to 500 kHz at temperatures from 10° to 100°C. For soft resin, dielectric dispersion was noticed for temperatures 20°C and above whereas for hard resin, appreciable dispersion could be observed beyond 60°C. For both fractions, nature of variation of Tan δ and dielectric loss with temperature and frequency was similar to those observed for shellac.

Cole-Cole diagrams of soft resin (Goswami, 1979) were different from those of hard fraction and shellac. For soft resin, two relaxation processes were observed for temperatures, from 10° to 40°C, and single process beyond 50°C. For hard resin, three processes were observed from 30° to 60°C, two processes at 70°C and single for 80°C and above. Many relaxation processes were attributed to relaxation of segments (combined

α and ß processes) and single process from relaxation of α process molecular orientation. The variation of ε_0 with temperature of two fractions was found similar to that of shellac. For soft and hard resin, glass-transition temperatures were found around 10° and 50°C and melting temperatures of fractions were found between 40° and 90°C. Higher ε_0 value of soft resin compared to those of hard resin between 10° and 70°C indicated that effective dipole moment per motional unit was greater than that of the other. Nearly equal $\in_0$ values for both hard resin and shellac, for temperatures below 40°C, suggested that number of dipoles present in both the resins were same. Relaxation time (which depends on molecular size) of shellac when compared to those of the two fractions at 80° and 90°C (for which complete Cole-Cole patterns were found in the order soft lac<shellac<hard lac. The molecular weights of the resins were also found in the same order (Refer Chapter 5). The decrease in the values of τ and α for fractions suggested some conformational rearrangements analogous to those reported for shellac.

Dielectric properties of hard-soft resin mixtures

Bhattacharya (1944) studied dielectric behaviour of different mixtures of hard and soft fractions at different frequencies and temperatures. Both ε' and ε'' values of 70:30 (parts) mixture of hard and soft fractions were in close agreement with those of lac (Goswami, 1979), Fig.7.6. The profile for soft fraction gradually approaches to that for hard fraction with increased addition of latter in hard-soft resin mixture and experimental points for 70:30 hard-soft resin mixture fitted well with those for shellac (Goswami, 1979). The Cole-Cole diagrams of this mixture also fitted well with those for shellac (Fig.7.7). Different dielectric parameters derived from these diagrams of 70:30 mixture at 80° and 90°C, obtained by Goswami (1979), Table 7.10. A good agreement was observed in values for 70:30 mixture of hard-soft fractions and of shellac. The results of dielectric studies confirmed the proposition that shellac is a physical mixture of 70:30 (parts) hard and soft fractions and corroborate with similar results obtained from spectral studies on different admixtures of soft and hard fractions (Goswami and Prasad, 1982).

Table 7.10. Comparison of different dielectric parameters of shellac and 70:30 hard-soft lac mixture at two temperatures derived from cole-cole diagrams

Temperature (°C)	Sample	$\in_0$	$\in_\infty$	$\Delta\varepsilon$	τ	α
80	Shellac	8.13	4.48	3.56	5.5×10^{-5}	0.61
	Hard-soft lac mixture	7.98	4.5	3.48	4.39 x 10-5	0.61
90	Shellac	7.85	4.74	3.11	8.74×10^{-6}	0.58
	Hard-soft lac mixture	7.72	4,64	3.08	8.26×10^{-6}	0.57

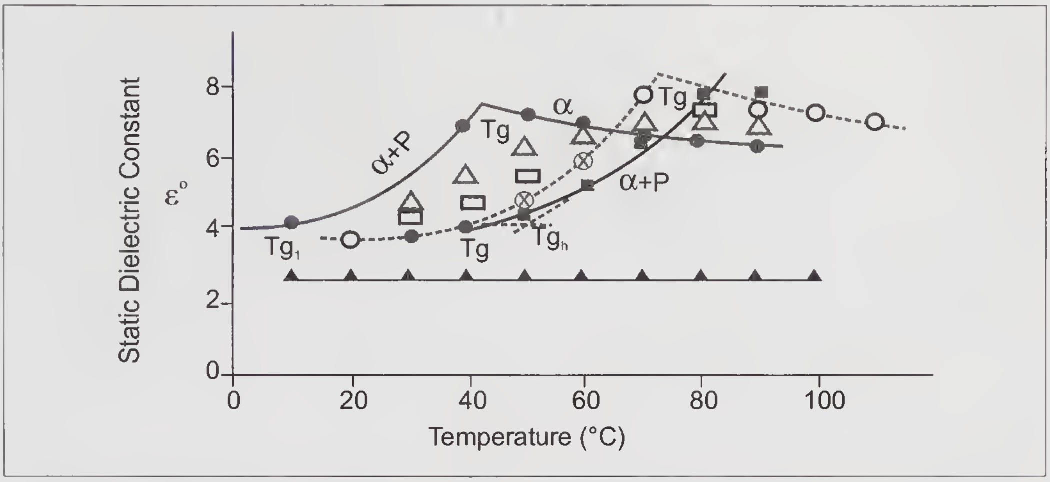

Fig. 7.6 Variation of static dielectric constant with temperature of soft lac (), hard resin (), shellac (o), 70:30 hard-soft resin mixture (x), 80:20 soft-hard resin mixture () and 50:50 hard:soft resin () mixtures.

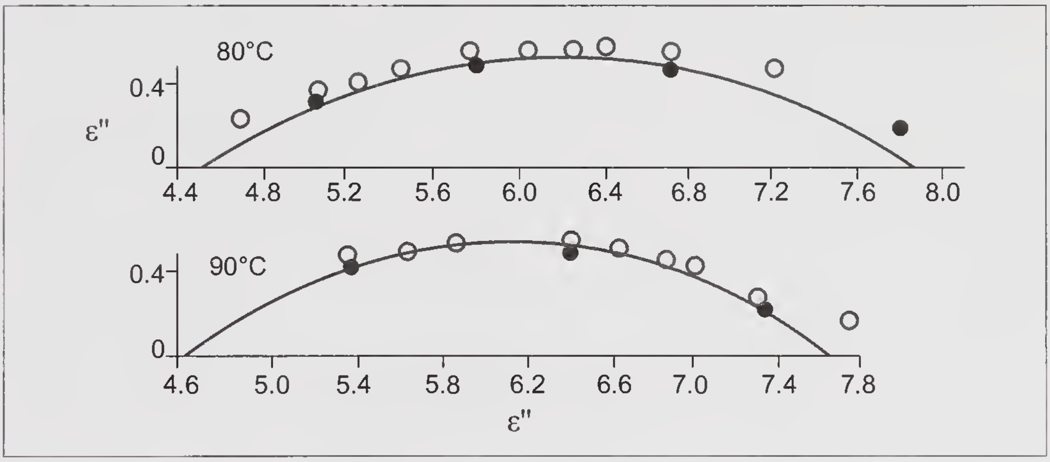

Fig. 7.7 Cole-cole plots of shellac (°) and of 70:30 hard-soft lack mixture (°) at 80 and 90°C.

Dipole moment of constituents

Bhattacharya (1942,1943 and 1944) determined dipole moments of soft and hard fractions of lac in 1,4-dioxan and also of palmitic, aleuritic acid and methyl-, ethyl esters of aleuritic acid in the same solvent. The temperature of the measurement for all was 25°C except for aleuritic acid, for which temperature was 40°C, due to its limited solubility in above solvent in lower temperature. The values of dipole moments of constituents of lac are of different types, Tables 7.11. The pure lac resin (hard resin) possessed highest value of dipole moment. Hard resin also showed higher ε_0 values (Fig.7.6) compared to shellac and soft fraction corroborating observation. The esterification of aleuritic acid did not show any appreciable change in dipole moment values.

Table 7.11. Dipole moments of constituents of lac

Materials	Solvent	Dipole moment (Debye)	Reference
Soft lac	1,4 Dioxane	4.61	Bhattacharya
Hard lack	1,4 Dioxane	7.45	Bhattacharya
Palmitic acid	1,4 Dioxane	1.75	Bhattacharya
Aleuritic acid	1,4 Dioxane	4.28	Bhattacharya
Methyl aleuritate	1,4 Dioxane	4.27	Bhattacharya

Shellac wax

Bhattacharya (1944) studied dielectric behaviour of shellac wax at different frequencies and temperatures. The lac wax used in this study was a purified product from commercial shellac wax, it was soluble in alcohol (it comprised 85% of the total). Dielectric constant remained almost constant up to 58°C and a sudden discontinuity was observed around 60°C for all frequencies studied. Nearly same value of dielectric constant was observed above 80°C for all frequencies. Softening and melting points of wax were determined between 67° and 83°C respectively, but temperature profiles (Bhattacharya, 1944) suggested that inner softening started little earlier (around 58° to 60°C), which may be termed as a transition temperature. Shellac wax (alcohol soluble) was reported to be mixture of primary alcohols of even number of carbon atoms from C_{26} to C_{36}. The dielectric properties of lac wax were interpreted to arise from dipole orientation. No conclusion, however, could be drawn from variation of power factor with temperature. Some characteristics of shellac wax are shown along with those of a few waxy materials, Table 7.12, which are used for impregnation of power capacitors.

Table 7.12. Characteristics of shellac-wax and a few other waxy materials*

Material	Melting point (°C)	ε_0	Tan δ	Volume resistivity (Ohm m)	Surface resistivity (Ohm)	Dielectric strength (kV/mm)
Shellac wax	83	2.78	0.0012	-	-	14-17
Paraffin wax*	50 to 55	2.2	0.0003-0.0007	10^{16}	10^{15}	20-25
Petrolatum*	-	-	0.0002	5×10^{12}	-	20

* Bhattacharya, 1944.

Dielectric behaviour of a few modified shellac compositions

Bhattacharya (1944) studied dielectric behaviour of shellac modified with urea and formaldehyde (SUF) and melamine and formaldehyde (SMF) as moulded discs in a wide range of frequency and temperature. Dielectric dispersion and dielectric loss-frequency profiles of both modified compositions were similar to those of shellac. Dielectric constant and dielectric loss values of the modified compositions were higher than shellac, indicating higher polarity of the modified compositions (Goswami, 1985). Transition temperatures, as revealed from ε_0 vs. temperature plots, were also similar to those of shellac (Goswami, 1985). The moulded discs could be crushed and reused for further moulding purpose, revealing that moulding compositions based on shellac were not truly thermosetting type (Bhattacharya, 1944). The Cole-Cole diagrams (Goswami, 1985) also revealed many relaxation processes below 70°C and one relaxation process above 70°C, similar to what were observed for shellac, confirming thermoplastic nature of shellac.

Lakshminarayanan and Gupta (1974) studied electrical and thermal properties of moulded discs prepared from (precipitated mass) blends of shellac-butylated melamine-formaldehyde and shellac-butylated urea-formaldehyde resins with and without fillers at different frequencies and temperatures (Lakshminarayanan and Gupta, 1979). Dielectric constant was found to decrease with increase in melamine resin content in composition. Since dielectric property of shellac is ascribed due to relaxation of hydroxyl groups, decrease in dielectric constant suggest a decrease in hydroxyl groups, which might have resulted due to reaction of OH groups of shellac and methylol groups of melamine resin.

Surface and volume resistivities of modified compositions were found lower than shellac. This might have resulted due to the presence of moisture and solvent molecules, which were trapped and were not removed while making discs. No considerable difference was, however, noticed. The modified compositions were reported better than shellac because of higher dielectric strength, discharge resistance, higher mechanical strength and moderate thermal conductivity (Lakshminarayanan and Gupta, 1978).

Dielectric properties of acetic ester of lac

Esterification was carried out by refluxing lac with acetic anhydride in the presence of pyridine as catalyst (Anon., 1947-48). The dielectric constant of ester was low when compared to lac and was in the range 3.5 to 5.8 at temperatures between 30° and 110°C and frequency range of 1 to 500 kHz. The D.C. conductance of the product was found lower than shellac. The maximum value of dielectric loss was also found low in the temperature range than that of shellac. The above observations were due to the reason that OH groups were no longer free after esterification.

Dielectric properties of lac-glycol ether

The study (Annon., 1947-48) was undertaken on the basis of the information that the insulating properties of lac-glycol ether improve with progressive polymerization and the electric strength of the fully polymerized product was reported to be high. Dielectric constant of unpolymerised lac-glycol ether was found to vary between 5.4 and 9.0 at temperatures between 30° and 70°C. The power factor and loss were not low. D.C. conductance was high. The acid value of the ether was 30. Consequently unpolymerised resin did not possess properties of a good dielectric.

Dielectric properties of lac-glycerine-linseed oil resin

Lac-glycerine-linseed oil composition was reported to possess low acid value and therefore, was expected to yield low dielectric loss. It was subsequently observed that acid value depended on the period of heating *i.e.*, presumably on the extent of polymerization (Annon., 1946-47). The acid and hydroxyl values of the samples drawn at various stages of polymerization did not show much change, but a marked variation in the viscosity was noticed. The conductivity also decreased enormously with the progress of polymerization. Dielectric loss did not show much variation with the time of polymerization. A shift in the power factor and dielectric loss curves was observed towards higher temperature, indicating possible polymerization of resin.

Dielectric properties of hydrolysed lac

Dielectric loss of lac was ascribed to arise from relaxation of OH groups. To have confirmatory evidence, dielectric properties of hydrolysed lac were studied (Annon., 1946-47). Dielectric constant as well as loss was found very high for hydrolysed lac than shellac as expected from the theoretical point of view. Precise measurements could not be performed due to high D.C. conductance.

Dielectric properties of the plasticised lac

Measurements carried out (Annon., 1949-50) revealed a shift of dielectric constant-temperature curves towards low temperature side, which was ascribed due to lowering of inner friction as the result of plasticisation. The shift was more with an increase in the amount of plasticiser in the system.

Tracking

Tracking is a process of formation of slow carbonized path on the surface of a solid (organic) insulating material due to passage of electric current along the surface when exposed to contaminated atmosphere of dust, salt and moisture. Failure of an electrical insulator due to tracking is an unwanted characteristic in electrical engineering. Shellac is, generally, known to possess anti-tracking property and it is this unique property by which it is distinguished from many synthetic resins which are known to form tracking under electric stress and in contaminated atmosphere in spite

Table 7.13. Tracking property of shellac and a few of shellac-based moulded discs

Sample	Contamination (0.1%)	Tracking index (Volts)	Remarks
Shellac (*kusmi*)	NH_4Cl	-	Melts, no failure
Shellac (*ranginee*)	NH_4Cl	-	Melts, no failure
Shellac-UF with fillers			
(i) wood flour	NH_4Cl	100-135	Tracking, erosion not
(ii) wood flour	NaCl	50	highTracking, less erosion
(iii) slate dust	NH_4Cl	-	No failure, high erosion
(iv) with asbestos	NH_4Cl	-	No failure, high erosion
Shellac-UF with saw dust filler	NH_4Cl	-	Erratic behaviour, occasional failure noticed, high erosion
Shellac-UF with saw dust filler	NaCl	195	Tracking, erosion depth not so high
Rubber-shellac composition	NaCl	-	No failure, small depth of erosion

Chakraborty and Bhattacharya, 1973.

of many good properties they possess. Chakraborty and Bhattacharya (1973) had made a brief study on the tracking property of shellac, shellac-urea-formaldehyde (with various fillers) and a few rubber (shellac modified) compositions in the form of moulded discs with an indigenously fabricated instrument (Table 7.13). Some studies were also made on the tracking property of SUF varnishes. Moulded discs of pure shellac (*kusmi* and *rangeeni*) did not exhibit tracking under normal conditions of the test even for 2 hr.The surface of the specimens, between electrodes, gradually melted due to heat produced by small electrical discharges and electrodes sank into the molten lac. SUF varnishes were found to possess improved tracking index values when compared with phenolformaldehyde resin.

The tracking resistance of films were prepared from seedlac, shellac and modified shellac varnishes (tests are performed on 50 micron thick films) following IS:8264-1976 and IS:10026-1982 with the help of a Beckman Insulation Tracking Test Set (Goswami, 1992). The tracking index values of seedlac and shellac varnishes were 224 and 256 volts respectively and of shellac films were found even better than those of synthetic resins widely used in electronic industries (Table 7.14).

Table 7.14. Tracking index values of a few synthetic resins along with that of shellac.

Resins	Sample nature	Tracking index (volts)
Shellac electrodes	Solid	No track formation, sink into the molten lac
Shellac	Varnish film	256
Shellac-epoxy	Varnish film (different compositions)	262-310
Shellac-polyvinylacetate	Varnish film (different compositions)	186-260
Polyphenylenesulphide	Solid	200-240
Phenol-formaldehyde	Solid	135
Ultem (polyetherimide)	Solid	160
Polyvinylacetate	Varnish film	174

Dielectric after-effects and Electrets

Electrets are electric analogues of magnets. These are sources of an electric field used in the instruments where high or low fields are required. The phenomenon of dielectric after effect concerns with the electrical changes in the body of the dielectric that persists after excitation voltage is removed. Schreiber (1913) studied exhaustively effect for sealing wax, shellac, ebonite, rosin, sulphur and paraffin. The results revealed that paraffin and sulphur show very little after-effect while responses of other materials although considerable, were in an order of decreasing intensity.

The fields of applications of electrets are electret microphones, vibrotransmitters, electrometers, electrostatic generators for focussing an electron beam in electron-ray tubes etc. The word ‘electret’ was used by Heaviside (1955) to denote a permanent electrified material having electrical charges of opposite sign at its extremities. Eguchi (1925) was the first to report preparation of electrets and showed that after-effects could be permanently set in a material by allowing a molten sample of dielectric to solidify in the presence of an electric field. Eguchi used mixtures of waxes and resins for the purpose.

The electret effect was reported in shellac wax. Pillai *et al.*(1972) have prepared shellac wax electrets with different polarizing fields and time. The nature of the surface charge formation and decay characteristics were also studied. It has been reported that surface charge density decays rapidly up to around 10 days after which it attains plateau. Both initial and final polarities of the surface charge as well as life-time of the electrets were dependent on both polarizing field and polarizing time. It was shown that the contribution to the surface charge of the electret was not merely a dipolar orientation but included contribution from other factors like stripping, moulding and spraying. Pan (1976) reported X-ray diffraction patterns of electrets prepared using sealing-wax.

Dielectric parameters of shellac and a few other natural resins

Dielectric relaxation behaviour of natural resins Manila copal, mastic, dammar was studied by Bhattacharya (1946 and 1944) in the frequency range of 50 Hz to 500 kHz at different temperatures between 20° and 120°C, which was found similar to shellac. Goswami (1977 and 1982) also reported a transition from many relaxation proccsses in the solid state to single relaxation process in the liquid state during heating similar to what has been observed for shellac. The variation of static dielectric constant and loss measured at 1 kHz with temperature of shellac, Manila copal, mastic and dammar has been shown in Fig.7.8 using data obtained by Goswami (1979,1977 and 1982) and Bhattacharya (1946 and 1944) respectively. Static dielectric constant and loss of shellac were higher compared to other natural resins revealing it to be more polar. Dielectric loss of dammar was found lowest among these natural resins. Both dielectric constant and loss of dammar were almost constant up to 100°C, indicating that its properties are more stable compared to other natural resins. Tan ä value of rosin (Bogoroditsky *et al.,* 1979) has been reported to attain a peak value of

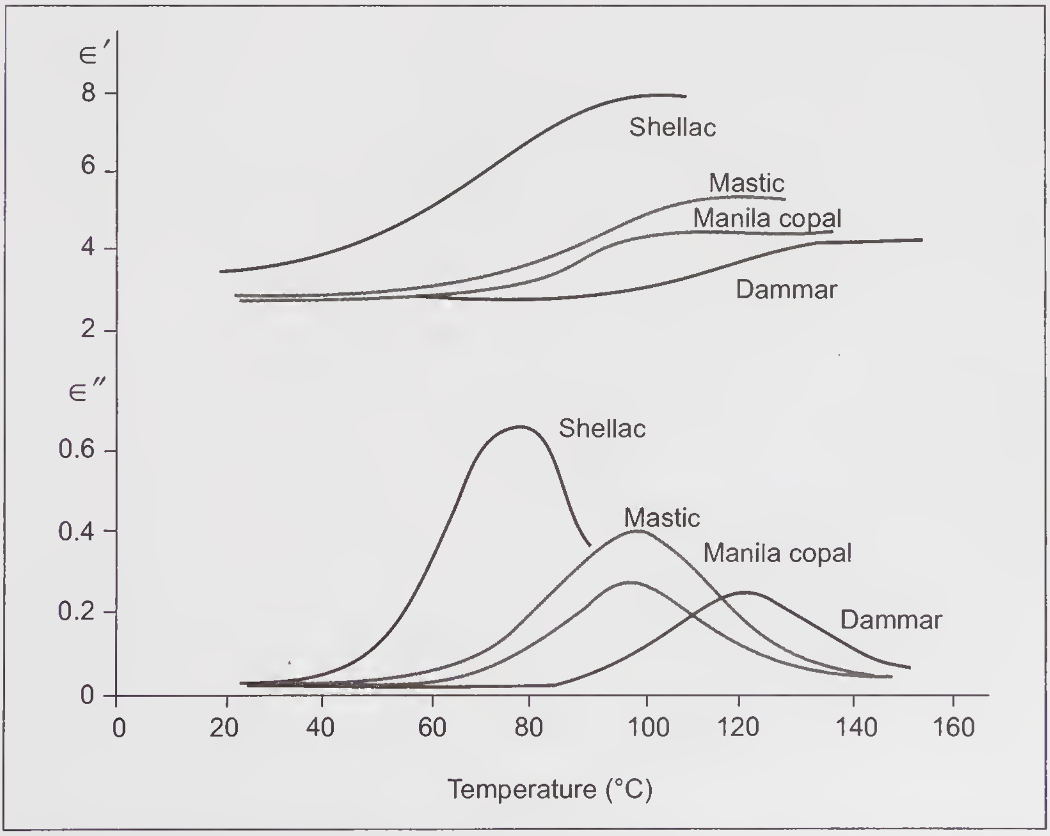

Fig. 7.8 Variation of static dielectric constant (∈′) and dielectric loss (∈″) with temperature of shellac and natural resins Manila copal, mastic, dammar

0.05 at 60°C, it shows a decline for a rise in temperature and a steep rise in its value again is observed above 100°C. Both dammar and rosin are available in our country like shellac and these natural resins also are in use in various paint and varnish formulations.

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8

Applications of Lac

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LAC possesses innumerable applications in various fields, the diversity is unmatched by any single resin natural or synthetic. This consists of traditional fields, which are being practised by artisans through centuries and researchers around the world have developed many more.

LAC IN SURFACE COATINGS

More than 50% consumption of shellac is in the surface coatings. The age-old applications of shellac in surface coatings are believed to be due to the following qualities:

- Its ability to produce smooth, decorative and durable films from alcoholic solutions, which dry rapidly.
- Excellent adhesion and bonding material for a wide variety of surfaces, exhibiting high gloss and hardness.
- Ultraviolet resistance of films.
- Excellent compatibility with cellulosic materials and hence capable of yielding laminated products.
- Superb thermal plasticity, ready fusibility coupled with ability to absorb large amount of fillers.
- Ability of film formation of alkaline solution
- Unique dielectric properties
- Non-toxic nature and renewable resources.

However, innumerable formulations were developed (Sankaranarayanan, 1977) most of these were not scientifically recorded in early times. Inventors started recording their claims through patent applications about a century ago. Though we find a British patent application on aqueous shellac solution in 1901 (Sooter), shellac-based patent on leather finishing was recorded as early as in 1845 (*op. cit.* Sankaranarayanan, 1977).

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Shellac based varnish, lacquer and polish formulations

Lacquer and Lacquerware

The Indian lacquer is based on shellac. Manufacturing of lac-based lacquers and application on wooden articles are unique in technique and are being practised in the country for centuries. The use of lac for the purpose has been mentioned in *Ain-E-Akbari* (1590) in Travelogues of Dutchman J.H. van Linscholen (1596) and of an Englishman Terry (1655) (*op. cit.* Sankaranarayanan, 1977). Collections of Indian Lacquer wares in the famous museums all over the world are indicative of appreciation of exquisiteness of their styles and colour designs.

Use of shellac as sealer and primer in the paint and lacquer trades is widely practised (Anon., 1934). Varnishes/lacquers are generally prepared by dissolving a resinous substance in a solvent medium. After application on the substrate, the solvent evaporates leaving a solid hard film on surface of substrate. These varnishes are applied on wood and metal surfaces for protective as well as decorative purposes. There are two types of lac-based lacquers:

(*i*) 'solvent less lacquer' and is applied with differently coloured lacquering sticks. These are prepared by fusing shellac, (mixing) white pigment (generally lithophone) and various water-soluble dyes. The coloured-fused mass, is drawn into sticks of suitable sizes while hot.

(*ii*) *French polish* is based on the solvent, the evaporation of which when applied on the surface, provides a protective and decorative coating of shellac. Maiti and Rahman (1986) reported various uses of shellac.

Air-drying type varnish

Simple air-drying type brush-able and spray-able varnish compositions were developed based on shellac, denatured alcohol, n-butyl alcohol and plasticisers (Venugopalan and Sen, 1948 and Bhattacharya, 1947). High gloss polish can be obtained based on shellac, ethyl acetate and whiting (Willkie, 1922). Blush- and heat-resistant shellac varnishes were developed based on shellac, alcohol, urea or thiourea (Venugopalan *et al.*, 1934). Thiourea was found superior to urea in imparting blush resistance but films were more brittle. Addition of 0.5 to 1% of 10% solution of sulphur monochloride in carbon tetrachloride to shellac varnish improves water resistance (Venugopalan, 1934). Improvement in water resistance of shellac has also been reported by boiling its alcoholic solution under reflux with melamine, till it goes completely into solution (Anon., 1940-41). Improvement in weather and water resistance of shellac films has been reported by addition of 1% urea and 5% nitrocellulose to dewaxed lac varnishes (Bruins, 1936); plasticising (with TPP) shellac varnish with thiourea (Anon., 1934-35), incorporation of polyamides (obtained by the condensation of dimerised vegetable oil acids with ethylene diamines)

(Nordgren *et al.*, 1951). Incorporation of allyl starch improves heat and solvent resistance as well as hardness of shellac (Nordgren, 1951a). Deoiled bees wax has been reported to improve elasticity and water resistance of shellac varnish. Incorporation of 0.5 to 5% of maleic acid into shellac varnish was found to yield hard, adherent and flexible films, which do not 'green' copper on baking.

Improved abrasion resistance of films was obtained (Zinsser and Co., USA) when dewaxed shellac varnish in alcohol was treated with urea/formaldehyde resin dissolved in a mixture of alcohol and aromatic hydrocarbon and acid catalyst such as dimethyl pyrophosphorate. Light fast coloured spirit-based shellac varnishes (Schaldebache and Hahle, 1933) of various shades (with basic dye stuffs of the triaryl methane series), were prepared by incorpration of small quantities of strong acids or salts. Both spray-able and brush-able varnishes/lacquers were developed containing shellac and other natural resins (Kern, 1934 and Anon. 1935) like, copal, sandarac, accroid, dragon's blood, African copal, Manila copal, mastic, benzoin.

Melfolac—a heat and water-proof shellac varnish, for wooden furniture —was developed by modifying dewaxed shellac with butylated melamine formaldehyde resin (Kumar, 1966). Its performance compares favourably with those of synthetic resin based commercially available wood lacquers. The composition is sprayable. It yields a highly glossy attractive finish on wooden furniture. The varnish has already entered into commercial production. In view of the difficulty of obtaining methylated spirit, a spirit-less varnish composition was developed. This composition also produces a smooth, glossy and attractive finish on wooden furniture. A single-pack etch-primer composition was developed, which on application by brush, or by spray air-dried within an hour yielded hard, smooth and highly adherent coating on aluminium and other light metals. Air-dried films showed good holdout to topcoats and also showed resistance to acetone and alcohol.

Shellac-oil varnishes based on drying oils

Air-drying shellac varnishes were found to yield, in general, brittle films, which do not possess hardness and higher thermal resistance. Thus, varnishes could not have wider applications. A need for oil-based varnishes was conceived to achieve diversification of use of shellac in paint/varnish industries. It is well known that shellac does not go into solution in drying oils in normal conditions of varnish manufacture. A considerable amount of work was done on this aspect by researchers (Sabin, 1927). Aldis (1933) reported to dissolve shellac in a drying oil (linseed oil) by its prior heating to 380° to 390°C and then adding shellac in small lots maintaining temperature at 380°C. Shellac could be dissolved in linseed oil at a lower temperature of 320°C by heating under pressure. Sankaranarayanan (1946) reported that shellac could be incorporated into linseed oil at a comparatively lower temperature with prior cooking of oil with about 15% (on the weight of lac) of litharge or lead or an equivalent quantity of lead linoleate. Other oxides or carbonates of metals *viz.* those of sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) could be used in place of litharge (Sankaranarayanan, 1952-53). Metal soaps I., stearates of calcium (Ca), aluminium (Al) or zinc (Zn) could be used. Hard, glossy and elastic films were obtained resistant to useful solvents and weather from the oil varnishes (Venugopalan and Sen, 1948) containing shellac, red lead, linseed oil and solvent (white spirit, turpentine). To prepare varnishes based on reaction product of shellac and linseed oil using glycerine, rosin, ester gum etc. in place of litharge or metallic oxides were reported by Thakur and Bhattacharya, 1943; Bearn, 1923; Scott, 1928; Sankaranarayanan, 1949; Gupta, 1959; and Anon.1952-53. Oil varnishes drying within 2 hr yielding very hard and glossy films have been reported to be produced by reacting shellac, rosin, zinc oxide complex in stand oil (Aldis,1933). Shellac varnishes have also been prepared using other drying oils *e.g.*, tung oil (Nayudu, 1962), dehydrated castor oil. Mukherjee and Kumar (1982) developed a varnish composition based on lac, linseed oil having very good drying characteristics, which yielded hard, smooth, glossy and flexible films possessing good resistance to water and aromatic hydrocarbon solvents. The varnish could be pigmented to produce decorative paints. A coating composition based on linseed oil, ammonia, water, shellac and water-soluble fluorescent dyes has been reported (Grossman, 1954). Dioctyl phthalate and filler pigment could be used for improving covering properties.

Varnish compositions were prepared (Anon., 1938-39) based on shellac, acetic anhydride, glacial acetic acid, glycerine, p-tolune sulphonic acid, linseed oil, litharge, turpentine and cobalt linoleate. Reaction product yielded a glossy film in 6 hr and possesses good water resistance, adhesion, elasticity and scratch hardness.

Lac oil varnishes based on non-drying oils

Bhattacharya (1939) reported to have prepared a number of air-drying type shellac oil varnishes based on castor oil. The reactions were carried out at elevated temperature. The solubility of the compositions in alcohol decreased progressively due to the reaction. Addition of xylol in the reaction product helped solubility in white spirit. All varnishes prepared reported to air-dry satisfactorily within 24 hr. Ajmani (1945) reported to have prepared shellac-based varnishes in cashew-nut-shell liquid. The varnishes possessed satisfactory white spirit solubility and paints prepared exhibited excellent weather resistance. Pillai and Daw (1962) reported to have prepared black Japan-based on shellac, rosin, castor oil, turpentine, carbon black etc. Oil soluble shellac was prepared by reacting rosin, shellac and calcium oxide at elevated temperature. Esterification of shellac and rosin with glycerine is usual practice; the reaction product dissolves in oil at 270°C. Lac rosin glycerine ester is comparable with drying oil and stand oil (Anon., 1953-54) in all proportions when heated at 270°C. Shellac reported (Adams, 1933) to react with tannic acid and the reaction product dissolved in vegetable oils in the presence of high boiling solvents, which could be heated in ordinary containers at 200°C. Chopra and Sankaranarayanan (1965 and 1966) formulated lac-CNSL compositions for use as insulating varnish and as moulding material. Varnishes prepared chlorinated shellac-tung oil composition based on lac, tung oil and phenolic resins (Kundu and Kumar, 1966), when coated on paper or fabric, dried or baked, retained suppleness.

Water- based coating compositions

Shellac, as such, does not dissolve in water, but goes into solution in water in the presence of inorganic and organic bases like caustic soda (NaOH), sodium carbonate (Na,CO_3), ammonia (NH_3) , borax, triethanolamine, morpholine etc. Alternatively, shellac can be treated with base and then the product is dissolved in water. The shellac solutions in water could be prepared in a wide range of pH. Shellac is reported to improve film properties of synthetic polymers especially, in regard to leveling, removability, film continuity, gloss and adhesion. The maximum improvement has been reported for polystyrene and polyethylene (Brand *et al.*, 1957). Films—obtained from shellac solutions containing sodium salt of carboxylated methyl cellulose, solutions of aluminium, chromium or ferric sulphate—showed good water resistance without any deterioration in adhesion. The films were, however, uneven and translucent (Gidwani and Kamath, 1946). Preparation of aqueous shellac dispersions in the form of syrupy translucent liquid, based on dewaxed bleached lac, ammonium linoleate, linoleic acid and methyl cellulose, have been reported (Suter *et al.*, 1939). A few more dispersion compositions have been reported based on (*i*) shellac, ammonia, water, reaction product of 1 mole of oleyl alcohol and 20 mol ethylene oxide [Farbenindustrie, 1936] (*ii*) shellac, glycomonoacetate, reaction product of 1 mol oleyl alcohol and 20 mol ethylene oxide, quinoline and water (Farbenindustrie, 1936) and (*iii*) shellac, methyl acetone and triethanolamine (Anon., 1936), emulsion paint based on blend of shellac and acrylic resin with good water resistant property for cementitious surface (Ansari and Goswami, 2006).

Varnish (Coughlin, 1914) of improved lustre and flexibility was prepared based on shellac, ammonia and waste sulphite liquor. Water-proof damp resisting varnish [Parducci, 1935] was prepared which contained shellac (ammonical solution), latex, hardened gelatin (5% solution in alkali) stearmide (or stearnilide), viscose and dye (as required). Water lacquers (Aasheim, 1937) for floor polishes and leather dressings and for making wall-papers (washable) were produced by reacting shellac with mono-, di- or triethanolamine alone or mixed with homogeneous alkanolamines. The lacquers provided clear, odourless, water resistant elastic films. Transparent light fast lacquers (Geigy Alir, 1938), which can also be used as inks for printing on paper, were developed based on alcoholic shellac solution, saturated aqueous solution of sodium bicarbonate Na_2CO_3, concentrated ammonia NH_3, water H_2O and dye. On air-drying, the film becomes water- resistant and light fast. Heat resistant, moisture repellant lacquer (Christensene, 1933) for outdoor use was also developed containing shellac, ammonia (10%), leather gum, ethyl alcohol, diacetone alcohol, aldol (acetaldehyde or paraldehyde) and urea.

Non-inflammable fire resistant varnish (Fielder, 1943) has been developed for use on wood, paper, fabrics and similar materials. Neutral or slightly alkaline solutions of shellac in borax, ammonia or water-soluble organic amines were found to serve very well as dispersing agents for epoxy resins (epoxy equivalent 1 and mol.wt. 300 to 1500) Cockeram, 1959. These dispersions produced hard, tough impregnants for sheets and fibres. Polystyrene lattices containing shellac are produced by carrying out emulsion polymerization at a pH of 8 to 9.2, of latex containing at least 50% by weight of styrene compound in the presence of 0.2-7% of a non-ionic surfactant and 1 to 10% shellac, both expressed on the weight of the latex (Anon., 1960).

Shellac copolymer emulsions were prepared with styrene-butadiene (containing shellac, ammonia, water, potassium persulphate) Anon., 1965 and also with acrylates (Zdanowski *et al.*, 1962) (methyl C_3H_3, butyl C_4H_4, ethyl C_2H_2). The above emulsions produced hard elastic films of excellent electrical properties on baking at 150°C for 30 min. A graft polymer (Resart and Rose, *German Patent* as cited in Sankaranayanan 1977) was prepared based on shellac, dilute ammonia, oxygen gas, ethyl acrylate, ethylmethacrylate, glycidyl methacrylate, formaldehyde sodium sulphoxylate for use as lacquer for metal, leather, glass, paper, plastic, fabrics, textiles etc.

Water-soluble shellac, developed at this Institute was recommended to the Central Sugarcane Research Institute, Lucknow for use to prevent driage of cane sets. The initial experiments were reported to be successful (Anon., 1965-66). Dispersions containing graft polymers of vinyl acetate with ethylene-oxidized shellac have been reported (Arend, 1941). Aqueous dispersions showed good pigment compatibility, cold and heat resistance. These possessed also excellent adhesion and gloss. Small articles, were reported to be coated with shellac by electro-deposition (Arend, 1941) from colloidal solution in alkaline medium in the presence, preferably, of sulphates or chlorides, which increase conductivity and hence thickness of deposited shellac film.

Shellac has been reported to be soluble in aqueous sulphurous acid

(Bhattacharya and Verman, 1936). The product was air-dried with loss of sulphur dioxide yielding hard films insoluble in water. Soft films were obtained using water-soluble plasticising materials *viz.*, urea, glycerine etc. Adhesion, flexibility and hardness of films improved considerably by baking of films at 120°C. Even air-dried films reported resistant to dilute alkali and acids (except nitric acid) and common solvents. Lac was also reported soluble in aqueous solutions of sodium or ammonium bisulphate. The dissolution was rapid at 60° to 80°C. Air-dried films of sulphited lac were found resistant to mineral oils. Sharma and Sankaranarayanan (1968) reported water-thinned baking type finishes, based on modified alkyd shellac, with good adhesion and elasticity, water-thinned shellac primer for steel (Ghosh and Kumar, 1968) water-thinned shellac paints for internal decoration (Das Gupta *et al.*, 1982). Three compositions of water-thinable anticorrosive primers for steel surfaces were developed. These were based on lac-malenised linseed oil, lac-alkyd resin and lac-linseed oil fatty acid vehicles. Golz-berner (2001) reported to have invented an aqueous solution or dispersion with high shellac content. The shellac solution or dispersion can be used in the paint and varnish industry, the food industry and in cosmetics.

Other coating compositions

Shellac varnish has been used for protecting dental pulp from harmful effects of filling cement (Kruglykov *et al.*, 1969). Use of shellac has been reported in a variety of other formulations, *viz.*, in nail lacquer (Anon., 1982) as a protective lacquer for silvering mirrors (Bolewski *et al.*, 1972), for coating chairs in an electrostatic field (Timechko and Kharabaruk, 1968), in pressure spray containers for lacquer application (Huber, 1975), in formulation for self-polishing floor waxes (Weiss *et al.*, 1968), for lacquering rubber over shoes (Batabir *et al.*, 1969), weather resistant and anti-corrosive varnish based on shellac and CNSL (Chopra and Sankaranarayanan, 1965), shellac and asphalt based composition for improving durability and corrosion resistance (Baxter, 1966), self-degradable copying paper coating (Amamiya, 1974), as middle coat formulation (Kato, 1972) and intermediate coating material (Nozaki and Kodo, 1978), coating composition for textiles (Anon., 1966), coating for food and confectionery (Martin, 1966 and Hammond, 1965), as powder coating (Yakolev *et al.*, 1967; Vande Werff and Visser, 1972), coloured shellac-nitrocellulose coating composition for wood (Yaremchuk, 1969), liquid crystal based lacquer printing ink composition for temperature indication (Hesse *et al.*, 1973), in formulating mold-wash composition (Howells, 1973), tough, abrasion and chemical resistant formulations based on shellac and isocyanates for treating textiles and paper (Skeist *et al.*, 1965, 1966), etch primer formulation (Gupta and Sankaranarayanan, 1970), shellac-alkyd formulation (Chopra and Sankaranarayanan, 1967), single pack shellac etch primer containing malic acid for providing excellent flexibility, shelf-life and adhesion (Gupta and Sankaranarayanan, 1966), in formulating photosensitive composition (Obygraikin and Gurova, 1979), in xerographic binder plates (Cole, 1967), electrophotography recording composition (Sanders, 1967), in pigments for electrophotographic toners (Tsufuko *et al.*, 1976), etching in silicon and germanium plates (Anon., 1968), high gloss polishes for tiles (Tosllo, 1975), composition for grinding and polishing (Kalle, 1963), cleaning and preserving process for old wood articles (Sandu *et al.*, 2000), black correction paste for zincographical blocks (Beli and Tita, 2000), dewaxed shellac based floor cleaning composition (Juritsch, 1975), in multi-layer lacquer structure (Sheppard, 1962), alongwith other polishing agents (Balcunaite *et al.*, 1972 and Anon., 1966) ammoniacal shellac solution for developing coating composition for electrography (Sanders 1967; Kubota and Kojima, 1975 and Anon. 1975), lacquering caps for bottles (Hutch, 1934), coating of jute fabrics (Sengupta, 1968), shellac coatings over gold composition gilding (Anon., 1977), lacquered tins for packaging and storage of shellac (Kumar, 1973), can coating composition (Anon., 1999-2000), for finishing floor, stair treads, bowling alleys and toys [Modified shellac finishes for furnitures, floors and bowling alleys, SEPC, Kolkata] pattern paint composition for steel foundries (Das Gupta and Kumar, 1986).

LAC IN ELECTRICAL INDUSTRY

Use of shellac in electrical industries is being practised for more than a century. The first patent was taken on use of shellac in formulating hot melt insulating coating for telegraph insulators in 1852 (Anon., 1968). Spill (1870) developed a coating composition for insulation of telegraphic wires.

Shellac-based insulating varnishes

Insulating varnishes are widely used for coating of armatures/coils of electric motors, transformers, for finishing electrical components and also for preparing micanites, laminated products etc. Both air-drying and baking type of shellac-based varnishes are used depending on the nature of work.

Air-drying type: It is a common practice to use an alcoholic solution of shellac of desired concentration (25 to 40%). These varnishes air-dry quickly, form non-tacky, smooth, hard and adherent coating. Varnishes prepared with dewaxed shellac give dielectric strength of 40 to 48 kV/mm. Usually, wax-containing shellac varnishes give dielectric strength little lower than that obtained with dewaxed shellac. Fresh seedlac and shellac (*bhatta* or country made) have, however, observed to yield high dielectric strength of 62-80 kV/mm (Khanna *et al.,* 1986). Lac-based air-drying varnishes possess inadequate flexibility, suitable for application where ambient temperature does not rise above 65 to 75°C. The temperature rise beyond this, however, does not cause oozing of resin from coated surfaces.

Bhattacharya (1947) made an extensive study on the dielectric strength of various lac- based air-drying type varnishes under various conditions of testing. Baking of the films resulted in an increase in BDS values over those of air-dried films and a decrease in the BDS was noticed after conditioning of the films at 80% relative humidity. A general improvement in the dielectric strength of shellac was observed when it was modified with cashew-nut-shell (CNSL) liquid, urea-formaldehyde (UF) etc. The only defect with CNSL varnish was the poor flexibility of the baked films. Further, these varnishes were dark-coloured. Use of vacuum distilled CNSL was suggested to remove defect (Bhattacharya, 1947), which was, however, expected to raise cost of manufacturing. The Shellac-Urea-Formaldehyde varnishes were suggested for both air-drying and baking types of use. Baked films of Shellac-Urea-Formaldehyde varnishes were reported more brittle than those obtained from lac-CNSL varnishes.

Modification with synthetic resins

Reaction of dewaxed lemon shellac (60/65 parts) either with butylated melamine (40 parts)- or butylated urea-formaldehyde (35 parts) resins resulted in improvement in dielectric strength (Lakshminarayanan *et al.*, 1974). The BDS values for air-dried films were found 70 and 52 kV/mm respectively. Baking of the films at 95°C for 1 hr improved BDS to 90 and 85 kV/mm respectively for above varnishes. Lakshminarayanan and Gupta (1974) showed that measurement of dielectric strength and specific resistance could be used satisfactorily for the determination of optimum period of cure for the varnishes. An increase in BDS of the films was observed with the period of cure (maximum after 72 hr) and this was irrespective of the method of conditioning of the films. The SMF blends although resulted in high values of BDS, the films prepared from these varnishes, however, were not flexible, did not show thermal resistance more than 100°C and also did not possess any anti-tracking property. Goswami and Kumar (1984) observed that measurement of dissipation factor of the blends with time for shellac-epoxy resin and shellac-butylated melamine formaldehyde resins (Goswami and Kumar, 1984) could be satisfactorily used for determination of cure time.

Effect of plasticisers

Use of plasticisers in dewaxed lemon shellac varnishes have been reported to improve dielectric strength of films besides improving flexibility. Maximum BDS (80 kV/mm) was obtained with TCP (tricresylphosphate). Dielectric strength was found 68 to 70 kV/mm with DMP (dimethylphthalate) and DBP (dibutylphthalate). DMP treated shellac varnish showed good resistance to transformer oil (Goswami, 1982). Shellac-wax was found undesirable in plasticised shellac varnishes.

Baking type shellac insulating varnish

Air-drying type of shellac varnishes normally suffer from low thermal resistance and brittleness of films. These shortcomings were considerably overcome in baking-type shellac varnishes as these are generally based on reaction products of shellac and a drying oil. It is well known that shellac does not dissolve in drying oils under normal conditions, but when shellac is incorporated into drying oils in the presence of a metal oxide, it goes into solution. Based on the above findings a few compositions of baking-type insulating varnishes were developed; these were found soluble in cheap aromatic solvents and produced flexible films with improved electrical properties. Mukherjee *et al.*(1981) developed a baking-type shellac varnish based on DL shellac, double-boiled linseed oil, lime and litharge. The varnish possessed very good drying characteristics, compatibility with thinner, resistance to water, mineral and transformer oil and also showed high dielectric strength of 84 kV/mm. Recently, a few baking type insulating varnish compositions have been developed based on the ordinary shellac, some quantity of alkyd, polyamide resins and commonly used solvents (Goswami 2001, Goswami *et al.* 2009). The process of manufacturing is simple as it involves only blending of solutions of shellac and synthetic resins in solvent system under certain conditions. The process does not liberate any by-product and hence, the manufacturer need not worry about its disposal. The films possess high dielectric strength (85-95 kV/mm) in air and the property does not deteriorate much after immersion in water

Table 8.1. Characteristics of anti-tracking baking-type high thermal and water- resistant insulating varnish based on shellac.

Items	Characteristics of anti-tracking
Baking schedule	90/60 min at 150/175°C
Finish	Smooth, non-tacky, film glossy, uniform, hard
Effect of varnish on enameled wire (pencil hardness)	>16 (>6H)
Dielectric strength (kV/mm)In airIn air after immersion in water for 24hr	85-95 75-80
Greening of copper	Does not green
Resistance to tracking test as per IS:10026-1982	Passes, showed increased resistance towards tracking
Resistance to transformer oil (visual)	Passes
Thermal rating (by TGA)	178°C
Scratch hardness (g)	>2000
Specific gravity	0.91
Test for flexibility (3 mm mandrel)	Passes

(Goswami, 2001)

for 24 hrs (75-80 kV/mm) Table 8.1. So far, no baking shellac-based varnish has been reported to possess such high resistance towards water. The performance of the varnishes was found to be satisfactory when applied on the coils of 3.3 kV 400 H.P., 750 kW 3.3 kV electric motors.

Saha and Banerjee (1984) developed a process for the preparation of shellac bond powder for utilization in manufacture of laminated micanite sheets and other types of micanites.

Other uses

Various other uses are in formulations of non-inflammable insulating compound (Parkes, 1882), coating composition for protection of electrical components against varying humidity and temperature (Pye, 1949), damp-proofing of electrical condensers (Robert Bosch, 1928), finishing (safety) varnish for electrical condenser (Grimey, 1934), oil-proof insulating varnish (Nordmann, 1934), finishing varnish for field magnets (Kempton and Thomas, 1939), barrier layer for selenium rectifiers (Tueker, 1919), electric resistance elements (Marbury, 1921), insulating paints (Honig, 1896), alkyd substitute particularly for electrical insulation (Gidvani and Kamath, 1944), shellac alkyd insulation and impregnating varnish (Carrick *et al.,* 1947), electrical wire enamels (Verman, 1935), dispersion coatings for enameled wires, non-inflammable insulating compound (Zdanowski *et al.*, 1962), solvent-less coil insulation (Hancock and Silver, 1862), improved bond for hard and moulding micanites (Ghosh and Venugopalan, 1958), solvent-less lamination of mica (Tinnerholm and Paterson, 1984 and Edgecomb, 1917), flexible laminated insulators (Mc Coy, 1919), laminated insulators for oil filled electrical devices (Segar, 1933), tracking resistant laminated insulators (Warren and Smith, 1928), laminated insulating tubes (Reynders, 1915), mica insulators for spark plugs (Mosler and Morgolin, 1919), acid-resistant insulating material (Rhodes, 1882), fire proof insulating compound (Menningen, 1915), improved elastic binder for insulating material (Lake, 1890 and Knudson, 1890), composition for electrical battery container and sheet (Abrey, 1926) and composition for commutators (Tazewell, 1916).

LAC IN ADHESIVE AND CEMENT FORMULATIONS

Various adhesive/cement formulations (Sankaranarayanan, 1970 and Neuton, 1850) were developed based on lac and hydrolysed lac. The description of the work done on use of shellac as an adhesive in the nineteenth century is as given here. The first patent taken on any use of shellac was on the formulation of shellac-rubber cement by Neuton (1850). Bateman (1864) developed an oil and waterproof composition for uniting 2 pieces of leather and fabric containing shellac. Lee (1864) developed a thermoplastic cement composition for binding brick with wood for buildings, wood, slabs or ornamental tiles for flooring, marble, glass, pottery metal, ivory, pearl, leather, caulking of ships and other structures.

Shellac was also used in formulating an adhesive composition (Johnson, 1969) to stick to another surface coated with it, which did not require any solvent or water to develop stickiness. Duncan (1853) developed a series of thermoplastic cements based on shellac and gutta-percha for uniting silk with other fine fabrics, jointing leather, wood, caulking of ships, metals, glass, stone earthen-wares etc. Rhodes (1879) developed cement compositions based on shellac, asbestos, *gutta percha* and caoutchoue for making fast-and-immovable joints for lining cocks, valves which are resistant to a variety of chemicals and solvents. Swanzy and Clewer (1898) developed shellac based water-proof jointing cements for buoyancy apparatus such as air tanks for boats, life-buoys etc. Longbottom and Longbottom (1865) developed flexible, water-, fire- and insect-proof cement suitable for manufacture of carpets, floor cloth, felt, wallpaper etc. Mayall (1865) developed a cement composition for use in the manufacturing of hoses (for uniting fabrics to rubber tubes). Codet-Negrier (1857) developed flexible, waterproof and heat-resistant leather cement.

In the twentieth century also, in spite of the availability of the synthetic substitutes, interest on shellac in developing adhesive/cement compositions persisted among inventors. Several compositions were developed for jointing glass to glass, glass to metal and metal to metal (Anon., 1941-42), heat-and-water resistant adhesive (Stille, 1932) for any type of surfaces that withstand 130° C, especially for binding grinding wheel to metallic mounting on a rotating shaft, water-proof, non-toxic thermoplastic adhesive of strong bonding strength even to smooth surfaces such as cellophane (Kallander, 1939), alkali-resistant varnish for laying linoleum etc. on concrete (Jenkins, 1924), synthetic rubber-based cement suitable for preparation of gas musk (Sarbach, 1944), boiling water-resistant cement for fabrics (Plasterer, 1923), non-inflammable adhesive for sticking of rubber for cycle, motor-tyres, leather trades (Pichon, 1909), hydrolysed lac-based multipurpose adhesive (Sen and Venugopalan, 1948) resistant to steam and boiling water for bonding glass to glass, glass to metal, metal to metal, porcelain to porcelain, flexible micanite etc., water white transparent adhesive suitable for use in manufacture of safety glass and laminated articles (Venugopalan, 1956 and Annon.,1936-37), adhesive for bolts and nuts (Anon., 1959-60), for fixing bristles in brushes (Ghosh and Venugopalan, 1958), water-proof adhesive for manufacturing of leather driving belts (Anon., 1935), adhesive for laying aluminium on air-plane fabric (Bradley, 1919), adhesive for bonding leather, wood and paper (Bhattacharya, 1961), for pasting linoleum to walls (Gregoire, 1935), adhesive based on shellac and phenolic resin for glass (Tsuji *et al.*, 1954), glass to metal joining (Annon., 1953), in electric bulb manufacturing, adhesive based on shellac, hydrolysed lac for joining glass and porcelain (Ghosh and Venugopalan, 1958), gasket shellac compound (Dufoa, 1922) of improved adhesion, flexibility, shock and oil resistance, for steam flange joint (Brown, 1917), a cementing composition for application on metal surfaces in steam engines (Dufoa, 1922), steam pipes, receptacles and other conduits like water pipes for sealing a joint or crevice to stop leaking, adhesive for fixing lenses (spectacles) to their mounts (Brown, 1917), pipe jointing compound based on lead chloride, ferric oxide and shellac (Rottmeyer, 1935), shellac-based liquid cement for jointing/sealing with increased resistance to skinning (Hirsch, 1957), and also packing paste (Ford, 1952) suitable for application to threaded or rolled joints, adhesive for drawing steel tubing which does not scratch tube (Steel, 1948), adhesive for joining wire to carbon or graphite brushes (Narayan, 1948), adhesive for bonding paper with metal foil (Tsceike, 1921), dry mounting tissues (Anon., 1956-57; 1958), cement for coating backs of tips of billiard cues (Dunkerley and Dunkerley, 1908), as water-proof reinforcing back for maps, charts etc. (Collins, 1924), for fixing loudspeaker paper cones to metal parts (Venugopalan, 1956), fusible adhesive for sticking gold leaf to paper support (Wolfe, 1934), extender for phenol formaldehyde adhesive for plywood (Jain and Gupta, 1965), hydrolysed lac-based adhesive paste for sealing cracks in metals and castings for effecting metal to metal bond (Venugopalan, 1956), dry mounting adhesive creams for photographs (Perez, 1915), electrical insulating cement (Barringer, 1922), solvent-less general purpose cement for joining core laminations of electrical instruments (Venugopalan, 1956 and Murty, 1945), cement for bonding abrasive grains to steel (Krug, 1924), cement for fixing bakelite mouldings to metals (Kamath, 1944), cement for fixing diamond to holder for polishing purposes (Coleman, 1921), cement for jointing optical lenses (Bishop, 1921), preparing De Khotinskey cement (Anon., 1963), preparation of Peltmans cement for filling, joining and for protecting against moisture of munitions (Venugopalan, 1956).

Shellac is ascribed to be the only satisfactory binding material (Kulpmann, 1934) for cutting wheels for marble, granite, shale, terrazzo and concrete. It is used in the manufacture of abrasive discs of improved hardness and reduced porosity (King, 1919), quick wearing grinding wheels, which continuously expose fresh surfaces of abrasive grains (Power, 1922), as binder of carborundum grains for production detachable ‘teeth’ for stone-saws (Russ, 1916), carpenter’s abrasive stone (Anon., 1956-57), grinding stones for sharpening razors and surgical instruments (Stean, 1921).

Shellac varnishes in alcohol modified with urea or melamine formaldehyde may be used for preparation of laminated boards of paper, canvas, asbestos etc. of good mechanical and shock resistance (Anon., 1940-41), further uses of shellac have been reported in adhesive for lamination of jute boards (Anon., 1943 and MacMillan, 1945) for use in tea chests, for supplying dropping equipment, racking, paneling boards (Anon.,1953-54), paper laminated boards (Venugopalan and Sen, 1948), laminated fibre boards (Mc Clain, 1921), duplex boards (Ford, 1920) shellac adhesives (both spirit and water-based) for manufacturing plywood (Venugopalan and Sen, 1948), boiling water-resistant plywood (Anon., 1958-59), as thermoplastic adhesive for bonding wood to paper in formation of special floor coverings (Pederson, 1915), as bond for production of laminated fabric with multiple layers of tissue paper for production of diaphragms of gramophones (Cookson, 1917), as a binder and finishing material for films of inner skins of poplar trees for production of acoustic diaphragms (Drummon, 1923), hard composition of sealing corks of bottles (Venugopalan, 1956), as bond for lamination of vulcanized fibre paper for manufacturing steering wheel rims (Esthurn, 1917), rubber-less power transmission belt (Wood, 1918), puncture sealing compound for pneumatic tyres (Cleghorn, 1924), varieties of sealing waxes (Becher, 1934 and Bhowmik, 1955), cold sealing wax (Hochgesand, 1937), lightable sealing wax (Nadler and Kinghorn, 1923), liquid sealing wax (Galludo, 1933), non-inflammable sealing wax for electrical insulation (Snelling, 1917), strain-resistant sealing wax (Lack, 1926), sealing wax as candles (Hohmann, 1923; Mischkulnig, 1924; Weiss, 1925; Schiepe, 1926; and Bornand, 1926) transparent sealing wax (Prikelmeyer, 1926), wax engravers (Anon., 1963-64), bonding polythene to paper (Studencki *et al.,* 1981), adhesive for bonding iron, brass and copper substrates (Prasad *et al.*, 1972), adhesive for bonding mica rectifier pieces (Shibayama *et al.,* 1974) based on shellac, epoxy and melamine resins, adhesive topcoat for polyethylene laminates based on shellac, nitrocellulose, mixture of ethyl alcohol and propyl acetate (Rudolph and Mc Shane, 1968), shellac along with a fire retarder for preparing fire-resistant laminates (Marshal and Kukleies, 1977), hot-melt adhesive with high-bonding strength (Annon., 1993-94), fibre-composite based on renewable raw materials (Ulrich, 2000), as a binder for making paste for soldering aluminium and to increase protective and fluxing properties (Kurguzov *et al.*, 1975), as a binder for abrasive tools (Amanyan and Pakayev-Povodator, 1967).

LAC: MISCELLANEOUS APPLICATIONS

Manufacturing lac bangles is a traditional industry in this county, although synthetic plastics have reduced quantum of use, but a large quantity is still being used for bangle making in north Bihar, Jaipur in Rajasthan, Benaras in Uttar Pradesh, Hyderabad in Andhra Pradesh, and West Bengal. A considerable amount of shellac is used in metal enamelling. Moradabad and Jaipur are the chief centres for such an art craft. Shellac is also used by gold- and silver- smiths for filling in hollow jewelry and for fixing diamond on stiffer bases for cutting, polishing and for fixing metal plates for engraving and working. Ancient ceramics and old glass are protected by shellac films (Anon., 1936), shellac is used for hat stiffening (Ulrich, 2000), preparation of hat and leather dressings (Dorner, 1934), (modified) shellac for priming and finishing of metals, hot spraying of shellac (Kurguzov *et al.*, 1975), shellac floor polish (Amanyan and Pakayev-Povodator, 1967). The various uses of shellac and modified shellac have also been recorded for manufacturing extrusion moulded articles (Anon., 2000), fibre composite material based on renewable raw materials (Ulrich, 2000), non-foaming, non-viscous alcohol-free water-based pressurized hair spray (Anon., 1994), shellac resorcinol paraformaldehyde gelled cation-exchange resin (Sharma *et al.*, 1991), as binder for making pencils for use at high temperature (Volkove *et al.*, 1976), as an ingredient in formulations of hair spray, shampoos (Morelle, 1966), for production of stable emulsifiable gel for protecting metals – like brass, aluminium, copper, nickel, galvanized metals against corrosion (Gallagher, 1966), for cleaning oil-coated aluminium surface (Eiland, 1969), for creating artificial turbidity in soft-drink formulations (Nishiyama and Toda, 1973), in certain de-icing and anti-icing compositions (Sewell, 1981), as dispersant for colouring compositions for polyesters (Oori *et al.*, 1975), for improving air permeability of soils in organic fertilizers (Oki *et al.*, 1970), for improving foaming characteristics of styrene polymers (Roth, 1959), for making foam plastics flame-proof (Shashtry *et al.*, 1959), along with corn starch for use as extrudates (Musahiro *et al.*, 2000), as a surface treating agent for water-repelling materials (Yokoyama and Sawada, 1978) in foam compositions for grinding and polishing (Kalle, 1963), in formulation for instant high-gloss polishes for tiles (Tosello, 1975) in foam compositions for grinding and polishing (Kalle, 1963) as a plasticiser in paste solder compositions for increasing strength of brazed joints (Grzhimalskii and Petrumin, 1969), as a binder for soldering aluminium and to improve protective and fluxing properties (Khrizman *et al.*, 1972), as coatings for food and confectionery (Martin, 1966) in liquid crystal based lacquers to be used in printing inks (Hesse *et al.*, 1973) coating composition for electrography (Kalle, 1963), etching of silicon and germanium plates (Anon., 1968) electrography recording compositions (Sanders, 1967), in xerographic binder plates (Cole, 1967), multipurpose glazing varnish for metal, plastic, earthen and terracotta surfaces (Goswami *et al.*, 2008).

Shellac modified with alkyd and urea in coating composition (Vaidya *et al.*, 1977) and shellac varnishes containing 3% urea have been reported to produce films with improved heat and blush resistance (Kundu *et al.*,1986), in small proportions urea behaves as an efficient accelerator for shellac, about 11% on the weight, producing most rapid curing [it behaves as a retarder (Mukherjee and Sankaranarayanan, 1968) with larger proportions], in formulating etch primers for metals (Sankaranarayanan, 1958) manufacturing of shellac moulding powders (Venugopalan *et al.*, 1940) and in injection moulding (Sankaranarayanan and Sen, 1941) preparation of cold enamel (light sensitive coating; Matsumoto and Kobayashi, 1935), varnish for photographic plates (Anon., 1940), formaldehyde-free composite board based on sticklac and *arhar* stick particles (Sao *et al.,* 2008).

In leather finishes

Use of shellac in leather finishing (Sankaranarayanan, 1978 and Forster, 1844) was known to artisans over centuries and has been an old practice. The oldest patent taken on any use of lac was on a composition for waterproof coating for leather on fabric in 1844 by Foster (1844). Other uses of shellac were, dying and lacquering of leather (Anon., 1937), in formulating impregnating composition for toughening of leather, which prolongs life of leather (Gross, 1915), used for shoes and boots, another composition for carrying out impregnation under pressure or vacuum (Kemp and Kemp, 1864). ICI Ltd. (1935) also took a patent on impregnation and dressing agent for leather. Shellac was also used as an ingredient in formulating thermoplastic filler for holes in soles and boots (Elder, 1913), for hardening and water-proofing animal skins (Hartman, 1911), preventing shrinkage of leather (Lollar, 1938), stiffener for toes of shoes (Picker, 1916), powder glaze and paint for footwear (Medrowski, 1934), seasoning mixture for bleach-chrome tanned calf leather (Anon., 1932), surface application for leather goods where friction glazing is not practised, for formulating top coat for leather (Polo, 1920), gilding of leather, plastic etc. (Gibbons, 1941), high luster shoe dressings (Ratner, 1946), finish for upholstery leather (Gidvani, 1948), lacquer for leather (Collet and J.Coulon, 1935), water-thinned clear leather finishes (Angelino, 1951), enamel for leather boots and shoes (Hamilton, 1919), water dispersed pigmented leather finishes (Haon, 1940), emulsion coating for leather (Oakeshoff *et al.*, 1934), coloured coatings for leather (Fiala, 1951), finishing composition for kip butt splits leather (Anon., 1932), green bronze finish for leather (Weibor, 1932), solid-cleaning compound for publishing of leather goods (Szabo and Nits, 1936), finishing of rubber coated leather with shellac-cellulose based lacquer (Subranian *et al.*, 1962), grey leather finish (Meade and Friestedt, 1921), fixing composition for casein leather paints (Zuckermann and Metlitzkaya, 1938), cleaning composition for shoes (Anon., 1932), preparing liquid-shoe leather polishes (Hollis and Byron, 1893), leather shoe polishing cream (Paindavoine, 1933), bottom finishing of shoes (Anon., 1934), leather surface repair (Anon., 1942), finishing artificial leather (Anon.*a,* 1942), in manufacturing composition of artificial leather (Annon., 1908), for metallic finishing of leather along with graphite (Kedlaya and Mukherjee, 1973), as stiffener for chrome-tanned leather (Fekete and Poloskei, 1973) and as cleaning polish for leather (Humpa, 1975).

In pharmaceutical industry and controlled release

Use of lac and lac dye as an effective and valuable medicine is mentioned in *Atharva veda* (several thousand year old 'Wisdom of Ancient Truth' – seers of India) Anon., 1990 and Jhonston *et al.*, 1966. In the '*Veda*' that an extract of lac with water (contains mainly laccaic acid or lac dye) was widely used on open-wounds for quick healing and tissue generation. Use of lac for jointing broken bones was also common.

Shellac is, at present, used in coating of pharmaceutical products, as it is natural and non-toxic. The functions of shellac in this application are (Bold and Vynohradnik, 1966): to serve as a moisture barrier, protecting core ingredients; as an enteric coating; to control disintegration; as a granulating agent; As a finishing coat over wax, prior to printing of a trade mark.

The use includes coating of tablets, pills for resisting gastric juice *in vivo* and also acid resistant coating composition for tablets to protect against moisture and consequent decomposition (Nikolov, 1967; Signorino and Jamison, 1970 and 1971; Hess and Janseen, 1971 and Kawai *et al.,* 1974). Shellac-coated PAS (p-aminosalicyclic acid) tablets were found stable over 5 years with no reduction in drug activity (Minina *et al.,* 1978). Coated tablets were also found to retain bacterio-static action of drug for longer periods when compared with uncoated drug; different enzymes, aspirin have been reported to be coated with shellac (Kitajima *et al.,* 1970), composition based on shellac, castor oil, fatty acids, guaiac resin was used to coat pills, tablets for different dispersion in intestinal fluid (Swai and Iwayama, 1975). Shellac has been used to control disintegration of tablets and granules (Kaseem *et al.,* 1970), to prevent loss of colour of vitamin tablets and granules (Nikolov *et al.,* 1967), in compositions for oral administration (Ferris and Arambulo, 1974; Pescetti, 1976; Effinova and Minia, 1969; Selles and Cordoba, 1970; Smith, 1968 and Gstirner and Kaempgen-Botten, 1967), in formulation of shellac coated urea fertilizer for slow release (Bhowmik, 1980), a formulation based on shellac, ethyl cellulose was used to prevent hygroscopisity of PVP used for tablet coatings (Alam and Parrott, 1972), stabilizing vitamin C and B_6 granules for cattle food (Severa and Grunt, 1970; Limmatvapirat *et al.,* 2004 and Chang *et al.*, 1990). Modified hydrolysed shellac has also been used for tablet coating (Limmatvapirat *et al.,* 2004). Use of shellac pseudolatex has been reported as an aqueous coating system for pellets (Chang *et al.*, 1990). Shellac has been reported to have a profound impact on stent-based rapamycin by protracting drug release (Euro patent, 2008).

In printing ink formulations

Shellac is being used in printing ink formulations since 1960s. It provides good wet-ability in ink formulations on to the surface and also for keeping tinctorial strength unchanged (Kaiser, 1974). Even in 2000, we came across patents of shellac based printing ink formulations. Shellac has been used in an anti-clogging water-thinned jet printing inks and jet-printing method

(Hirotaka, 2000). Inks have good storage stability and can give images with good water resistance. Shellac has been used in providing gloss, improving adhesion on the substrates and moisture resistance and formulating a number of flexographic ink formulations (Gary, 1967; Levechenko *et al.,* 1972; Hadert, 1969; Marx, 1972; Dzyuba *et al.,* 1976 and Satushev *et al.,* 1980). Shellac being non-toxic, it has been utilized in formulation of edible inks for printing on tablets and other food (Anon., 1982), water-borne laminating ink for use of plastic films for laminating (Anon., 1989), aqueous composition for use as printing ink (Anon., 1996) stencil spray printing inks and lacquers (Jones, 1933).

Shellac-rubber combinations

Shellac and modified shellacs have been found very useful compounding ingredients for natural and synthetic rubbers and these improve mechanical properties and aging characteristics of resulting compositions. Shellac/lac contains resin, wax and dye, which are usually compounded with rubber. Resin part is of low molecular weight and acts as a processing aid or plasticiser, which helps in compounding of various ingredients *viz.,* fillers into rubber. Wax also acts as plasticiser and it migrates to surface of rubber compositions forming protective film and helps delaying aging. The pigment present in lac is an anthraquinone derivative, known to act as an antioxidant (Saxena and Banerjee, 1963).

Scott (1945) first made elaborate study on the use of shellac as an ingredient in rubber composition. Shellac could be incorporated into raw rubber by normal process of mixing even in large amounts. It did not cause breakdown of rubber during mastication. Improvements in the properties of natural rubber on compounding with shellac are not so notable as in synthetic rubbers such as styrene-butadiene and nitrile. The properties improved are plasticity, modulus, tensile strength, tear resistance, hardness and aging characteristics. Changes in properties of rubber compounded with modified lacs were better compared to those with native shellac. In compositions containing large proportions of fillers or reinforcing agents (China clay or carbon black), addition of small amount of shellac made vulcanizate much harder. Shellac was found inert towards aging of vulcanized rubber and it was not detrimental.

Scientists reported use of shellac, modified shellac in compounding and processing of natural and synthetic rubbers both in the gum as well as in filled stocks. The research workers (Saxena, and Banerjee 1963, 1965, 1968; and Jose and Banerjee 1966, 1969) revealed improvement in tear resistance, tensile strength and hardness on the use of shellac (25%) in gum-stocks of oil-extended styrene butadiene rubber (SBR). The time of optimum cure was observed due to the addition of shellac-ester to styrene butadiene rubber, oil-extended and non-extended variety. Ageing characteristic of oil-extended SBR was reported to increase after incorporation of shellac. Incorporation of 40 parts of shellac in nitrile rubber caused reduction of curing rate and cross-linked density and incorporation in filled stocks of oil extended SBR resulted, in general an increase in modulus, tensile strength, tear resistance, hardness, resilience (Saxena and Banerjee, 1968). Mooney viscosity, scortch time, modulus, tear resistance and aging properties of natural rubber improved when blended with shellac or ethylene glycol modified shellac (Khanna, 1974; Singh and Khanna, 1973 and 1974). An improvement in tensile strength, tear resistance, hardness, hydrocarbon solvent resistance of SBR were noticed when the latter was compounded with shellac in place of coumarone-indene resin (Singh and Khanna, 1976). Use of Zn-salt of shellac in place of unmodified shellac has been reported to improve upon mechanical properties of both natural and SBR (Singh and Khanna, 1977). Dielectric properties of natural (Goswami *et al.,* 1988) and SBR (Lakhsminarayanan, and Gupta, 1977) have been reported to improve when shellac was compounded with them. Use of shellac as curing agent has also been reported for trans-1,4-polyisoprene (Anon., 1967).

Shellac-polymer/resin blends

Blending of different polymers is widely practised in polymer industry for obtaining improved properties of end products. Blending of shellac with different polymers has also been tried by researchers, which led to improvement in the resultant products. Synthetic resins, which were blended with shellac include phenolics, amino resins, epoxies, alkyds, polyurethanes, polyetherimides, nylons, polyesters, polycarbonates etc. (Maiti, 1990). Shellac and Polyvinyl chlorides (PVC) were mixed in different proportions for moulding. No proper incorporation was observed beyond 10% of PVC on the weight of shellac. Shellac-PVC moulded products were to be satisfactory. Incorporation of butyl ester of hydrolysed lac has been reported to reduce brittleness of PVC.

Attempts were made to develop insulating enamel composition for copper wire by heating shellac and polyamide (nylon) in m-cresol and then dissolving in solvent naptha. Satisfactory coating was found on copper wire after baking at 320°C for 90 sec. Films were resistant to transformer oil, methanol, xylol, xylene/toluene mixture. Nylon 66 after modification with paraformaldehyde and non-hydric alcohol in acidic condition was compatible with lac varnish and films obtained from blend showed flexibility and adhesion to tin, glass wood but no improvement was observed towards heat, water and chemical resistance. High thermal (~230°C) and water resistant films (after baking at elevated temperature) could be obtained by blending solutions of shellac with alkyd and polyamide resins (Goswami *et al.*, 2009). Smooth air-dried and baked (30 min at 150°C) films were obtained from blends of shellac and polyvinylalcohol. Films also possessed good adhesion and flexibility.

Baked films did not blush up to 24 hr of water immersion. Air-dried films, however, blushed after 1hr. Blending has also been carried out with polymers/resins giving varieties of products like, topcoat adhesive (nitrocellulose), wood varnish (amino resins, polyurethane), insulating coating (epoxy), coating for textile (PVC + polyvinyl acetate), adhesive for bonding mica (epoxy + melamine), printing ink (napthol formaldehyde) etc., Maiti, 1990.

Recently, shellac/sticklac has been used as filler along with synthetic resin based sheet moulding compound in manufacture of FRP sheets by hand lay-up technique and curing at room temperature. Shellac to the extent of 10% improved mechanical properties *e.g.,* tensile strength, tensile modulus, flexural strength and flexural modulus compared to those of synthetic resin-based sheets (Goswami *et al.,* 2004). The Izod impact strength of shellac-filled sheets was marginally lower than shellac-free sheets. Arc resistance of shellac-filled sheets (70 sec) was, however, lower than synthetic resin-based sheets (90 sec). Higher arc resistance was obtained when gummy mass (waste obtained during preparation of aleuritic acid from seedlac) was used as filler along with sheet moulding compound. Sticklac (scraped lac) can be used in place of shellac for reducing cost. Thermal resistance of sheets was found dependent on the time of cure at room temperature. Thermal resistance tested after one day of preparation was 90°C and rose to 178°C after 57 days of curing. Besides, the sheets were resistant to water, kerosene oil, transformer oil, brine solution, dilute acid etc. Pigmented sheets possessed attractive finish and glossy appearance. Tea coasters have been prepared with shellac filled synthetic resin-fibre glass (CSM) mats. Shellac-synthetic resin based jute reinforced sheets have also been prepared. Shellac based SMC compound has also been used to coat on plywood to provide an attractive finish to furniture (Goswami *et al.,* 2003).

Attempts were also made to prepare sheets by using shellac-based high thermal resistant insulating varnishes by hand lay-up technique and curing at elevated temperature. Finish of such sheets was non-glossy. Mechanical properties of such sheets were found inferior compared to those prepared by curing in at room temperature (Goswami, 2001).

USE OF LAC DYE AND LAC WAX

About 100 tonnes of recoverable lac dye, dissolved in lac effluents, is lost every year in our country, even though final product ('pure' lac dye) is expected to fetch additional income for lac processing units. However, a sustained demand for lac dye (Table 8.2) has to be created by combined efforts of researchers and entrepreneurs.

Lac dye is sparingly soluble in cold water but highly soluble in boiling water. It is also soluble in methyl alcohol, amyl alcohol, acetone, acetic

Table 8.2. Characteristics of lac dye.

Composition of lac dye	Characteristic
Melting point	Above 230°C, with charring
Volatile matter at 135°C	6 to 7%
Acid value	234 to 240
Ash content	1% (maximum)
Solubility in water:	
Cold water	50 to 55%
Boiling / hot water	98 %

acid, dimethyl formamide and formic acid but insoluble in diethyl ether, chloroform and benzene. It turns orange-red in aqueous acid solution and reddish-violet in alkaline solution, but alkaline solution is unstable and decomposes rapidly. The dye also dissolves freely in cold sulphuric acid (H_2SO_4) with a beautiful carmine-red colour. Hydrochloride acid solution of lac dye can dye wool and silk directly, giving a beautiful orange-red shade, which is fast to light. Different attractive shades may be obtained by using different mordants (Table 8.3). The amount of mordant varies from 2 to 5% on the weight of material to be dyed and also the shade

Table 8.3. Different mordants to obtain different shades of lac dye.

Mordant	Shade
Copper oxide – ammonia	Bluish violet
Lead acetate	Bright to dark reddish
Lead acetate, followed by aqueous hydrogen sulphide (H_2S) solution	Violet (depending on duration of treatment); deep violet
Potassium dichromate	Reddish-yellow
Copper sulphate	Violet
Ferric chloride and subsequent treatment with hydrogen sulphide	Reddish-brown
Barium hydroxide	Dark carmine red
Calcium / barium chloride	Light carmine red
Copper sulphate, followed by hydrogen sulphide	Dark brown
Tin chloride and oxalic acid	Pink to begonia rose
Potash alum	Purple
Tin chloride / Oxalic acid / Potash alum	Vinacious purple
Ferrous sulphate	Mouse grey to sooty black
Potassium dichromate / Sulphuric acid	Brown
Potassium dichromate / Potassium hydrogen tartrate	Violet

required. Chitosan, a naturally occurring polymer has been used as a pre-treatment for dyeing cotton with lac dye. Dye produces violet colour on cotton fabrics, when dyed in an acidic medium. The wash fastness can be improved by use of mordants as well as by cross-linking treatment. Colour strength, colour co-ordinates and fastness of the dyed materials have been studied at the Central Institute for Cotton Technology, Mumbai.

After the present world-wide ban on azo-dyes, lac dye is expected to stage a come back; the dye being fast on animal (proteinaceous) fibres like wool and silk but not on vegetable (cellulosic) fibres like cotton. This is because animal fibres consist of amphoteric proteins, which have a natural affinity for acidic and basic groups-with which they combine by salt formation. To carry out diazotisation reactions with lac dye-amine-resorcinol as a naphthol component for purpose of dyeing cotton as well as synthetic fibres research is going on. Use of lac dye for dyeing synthetic fibres can open new vistas for the dye. Japan has started importing lac dye from China and Thailand for colouring fruit juice, hams, sausages, jams etc.

Lac dye is one of four commonly used insect dyes reported to have use in medieval Persia since 714 B C. Lac dye was the principal red dye used in classical Persian carpets and also to dye silk, yielding a range of colors from rose to purple. "Persian dye recipes were closely guarded secrets, passed from father to son". According to *Oriental Rugs*, 1937, the recipe was obtained by Mr Harris who is a dyer in India who claimed to be a descendant from 20 generations of dyers, originally from Tabriz. He stated the recipes came from a book of Persian dyes, originally owned by his grandfather. One of the recipes stated is as follows:

"*Persian Scarlet.* Take the lac colour, and if you choose a little cochineal for richness, and soak from 4 to 6 days; strain it in two cloths and add alum and a little turmeric; let it stand for 3 hr. Put wool in and steep for 24 hr, then boil for 2 hr. Take out the wool and add mineral acid; re-enter wool and boil 1 hr more. Wash 15 min. when cold, and dry in the shade" [*http://www.rugreview.com/orr/8-5-33.htm; www.roxanefarabi.com/Dye/Lac%20Dye%20in%20Medieval%20Persia.htm.*]

Lac wax is found to the extent of 4.0 to 5.5% in shellac and seedlac and to a slightly higher extent in sticklac. Both quality and quantity of lac wax in a particular sample depends upon the method of extraction. Wax recovered during production of dewaxed lac in alcoholic medium and dewaxed bleached lac in aqueous medium are better in quality as regards colour and hardness. Lac wax recovered from wash-water of lac factory and *kiri* or refuse lacs, is of inferior quality; it is soft, tacky and dark.

The presence of lac wax in lac-based surface coating compositions increases flexibility but decreases adhesion and water/heat resistance. Moreover, wax-free shellac is generally used to obtain clear solutions and decolourised/bleached lac is used for pale lacquers. The wax has a dielectric

Table 8.4. Current uses of shellac in different fields in Japan, United States of America and Germany

Field of application	Japan	United States of America	Germany
Paint and varnishes	Wood finishing, metal foil, sealers, leather, rubber, car tyres	–	–
Printing ink	Felt pen inks, binder for flexographic inks for paper, cardboard, non-toxic printing for food package	–	Inks for food and packaging
Electronics	Lamps, fluorescent lamps, insulating agent for parts, insulating varnish Insulation, adhesion, laminate	Lamp manufacture, glue for jointing metal with glass	Isolator coating, sockets of electrical lamps, PCB coating
Polishes	Fruits, furniture, floors, shoes	Stain sealer, wallboard primer, knot and sap sealer on wood	–
Tapes	Masking, adhesive paper tape	–	–
Pharmaceuticals	Coating for tablets; enteric (digestive fluid proof) coating for tablets, pills etc. Removing agent for medicinal odour	Enteric pills so that they do not dissolve in the stomach but in the lower intestine and also for 'time release' medication.	Coating of tablets
Food	Chestnuts, healthy foods glazing agent for chocolates, sweets, protective coating for oranges, lemons, apples etc. Binding agent for stamp inks for lemons, eggs, cheese. Barrier coating for feeds and seeds	Protective candy coating or glazes on candies. Approved by FDA as food safe coating when dissolved in pure ethanol (not denatured), coating of apples and other fruits	Coating of food materials

(continued to page 141...)

(concluded from page 140)

Field of application	Japan	United States of America	Germany
Cosmetics	Additive and binder for manicure, mascara, conditioning shampoo. Setting agent for hairspray, micro-encapsulation for perfumes.	–	Hairspray, eye shadow, micro-encapsulated perfumes
Rubstones	Grinding wheel	Grinding wheel	–
Adhesive	Crystals, precious stones, lenses	–	–
Leather	Protection, polishes	Leather finishing	Stiffening of leather
Wood products	Finishes, primers, polishes, sealers for the harmful gases (formalin etc.) that evaporates from building materials	Protective coatings for wood	–
Others	Felt hats, pyrotechnics, gunpowder, strippable paints, cards	Stiffening felt in hat manufacture	Textile

strength of 356-416 volts/mil. Among other naturally occurring waxes, lac wax is softer than carnauba or candelilla waxes but harder than bees wax or wool wax. Lac wax can serve as an import substitute for costly carnauba wax. However, natural waxes are being slowly replaced by petroleum waxes in several fields of utilization, like crayons, lubricants and industrial polishes etc.

Bioactive compound from constituent acid

Aleuritic acid (9,10,16 trihydroxy palmitic acid) is one of the major constituent acids of the lac resin. It is also one of the lac-based value-added export materials of the country. Since, this is used as a starting material for the syntheses of a variety of fine chemicals [*e.g.*, perfumery compounds *viz*., isoambrettolide (Majee *et al.,* 1998), civetone (Majee *et al.,* 1991), exaltone (Majee *et al.,* 1989) etc. and several other compounds, institute receives maximum request for transfer of technology for procedure of its isolation. The Institute has transferred technology on laboratory scale to a number of entrepreneurs. Isoambrettolide is used as a fixative in perfumery industry. The institute also possesses technology for its synthesis from aleuritic acid, which has been transferred to entrepreneurs.

Aleuritic acid was used as starting material for syntheses of other bioactive compounds like PGR analogues (Rajendran *et al.*, 1999 and Saha *et al.,* 2003, 2004), sex pheromone components (Majee and R.Ramani, 1993; Majee, 1998; Majee *et al.,* 1999 and Rao *et al.,* 1999), nematicide (Srivastava *et al.,* 2004) and thiazoles, oxadiazole, thiosemicarbazides (Majee, 1989).

Current applications of lac

According to a largest supplier of shellac in USA, the top 4 uses are in pharmaceutical, confectionery, hats and food coating (in descending order of use), protective coating for wood ranks number 8 (which is understandable because of availability of non-wood and laminated furniture). The applications which are in commercial exploitation in Japan, USA, Germany are given in Table 8.4 (the information have been collected from either extension booklet or from web site of leading shellac manufacturers/traders of the above countries).

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9

Shellac versus Synthetic Resins: the advantage and disadvantages

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IN 1907, Leo Backland, invented bakelite, the first plastic of the world. Next few decades, the world experienced invention of scores of new synthetic resins/polymers with amazing industrial applications. This, although, brought turbulence in the lac trade giving enough signal for uncertain future; the traders kept hope of survival through new uses and applications. The severe slump in production of lac in the country came in 1950s with the replacement of gramophone record by synthetics; the lac trade lost a considerable amount of consumption and export per annum in a jolt. The 'experts' of the trade opined no 'coramine' will save the trade and lac is set to move to oblivion. By this time another half century has passed, the world could not abandon shellac, because some of its rare qualities, although its consumption has become stabilized to about 20,000

Table 9.1 Advantages of shellac

Sl. No.	Natural resin shellac	Synthetic resins
1.	It is a natural organic resin produced by insect, thus resource is renewable.	These are petroleum derivatives, hence non-renewable resource.
2.	It provides a durable finish on wood. A damaged shellac finish can be easily renewed, by applying another coat without damaging the surface.	Synthetic resin based coatings cannot be removed easily due to polymerisation/chemical reaction. Sometimes a plane is required for removal of old coating. Chances of wood surface damage are high.
3.	Process of application (multiple coating) can be completed very fast, within a few hours.	Process of application of multiple coating of synthetic resin-based lacquers requires much longer time.

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Sl. No.	Natural resin shellac	Synthetic resins
4.	It possesses incredible adhesion on almost all surfaces, even glossy and finished surfaces.	Synthetic resin based coatings are sometimes strippable; do not adhere firmly on the surfaces.
5.	It dissolves in denatured ethyl alcohol. The solution has an antiseptic odour, which dissipates quickly as the product dries.	Synthetic resin based compositions are based on mostly oil/solvent, take longer time for drying, causes environment pollution.
6.	Shellac films are ultraviolet resistant, yellowing does not occur.	Many synthetic resin based coatings suffer from the defect of yellowing.
7.	Shellac can be applied at cold temperatures (40° F. and below).	Many synthetic resin based formulations suffers from this quality.
8.	The United States Food and Drug Administration has certified shellac as a protective glaze for candy and pharmaceuticals because of its non-toxic/hypoallergenic quality.	Many synthetic resins have harmful effects.
9.	For surface coating, it can be applied easily with a brush, pad, spray-gun, or wiping clothe. Brushes can be cleaned easily with household ammonia or alcohol.	Oil-based synthetic resin coating formulations require special cleaning agent (petroleum-based products with pungent smell).
10.	Processing of shellac does not liberate harmful chemicals.	Harmful chemical residues are left during processing of synthetic resins.
11.	Shellac possesses excellent compatibility with other finishes. It is even used as a sealer under polyurethane-based coatings. It is world's most effective stain and knot sealer.	This quality of shellac is generally unmatched.
12.	It enhances beauty of wood grain, brings out the richness of costly wood, finished surfaces look natural; 2 or more coats of shellac seal also odour in any type of porous surface.	No synthetic resin matches this quality of shellac.
13.	Shellac possesses excellent compatibility with cellulose materials	Specific resins are used for specific moulding jobs.

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Sl. No.	Natural resin shellac	Synthetic resins
	like wood, jute etc. and also inorganic materials like mica, fibre glass and hence high utility moulded materials can be prepared. Shellac is used for lamination work.	
14.	Due to its low melting point, it is used in various moulding work, as filler in the hollow space of jewellery, as hot melt adhesive for varieties of jobs, artworks and dry polishing of wooden articles. The moulded material can be melted again and put to use. Accepts large quantity of filler. It exhibits thermoplastic as well as thermosetting behaviour.	Artisans do not use synthetic resins for this purpose. Dry polishing quality of shellac is unique. Toxic fumes are released during moulding of synthetics.
15.	It can be stored under ordinary room temperature for about 2 years without much degradation in qualities.	Some synthetic resins polymerize within few months making them useless.
16.	It possesses excellent electrical insulation property like very high dielectric strength of 40 kV/mm, anti-tracking property with tracking index of 260V for shellac film of 50 μ thickness.	Few synthetic resins possess such high dielectric strength. Even high performance engineering thermoplastic polymers like PPS (200 to 240 V), polyetherimide (168V) possesses tracking index lower than shellac.
17.	It possesses versatile properties for use in surface coating, printing ink, slow release, adhesive, as sealant, fruit coating/glazing etc.	No single synthetic resin can match such versatility of shellac.
18.	Its constituent acid, aleuritic acid, is a source of fine chemicals (like isoambrettolide used in perfumery).	Such diversified quality is not available in synthetic resin.
19.	Available freely in the market in a paint shop.	Not freely available, beyond reach of rural mass.

tonnes; yet its natural origin provides it strength for its survival and revival amidst uneven competition from synthetics. It is a general curiosity to know the strength and weaknesses of shellac - "the parent of modern plastic", due to which it has survived through centuries (Tables 9.1 and 9.2).

Despite these short coming shellac is being used as an industrial raw material in varieties of formulations in surface coating, adhesive,

Table 9.2 Disadvantage of shellac

Sl. No.	Natural resin shellac	Synthetic resins
1.	Shellac does not have much variety to offer, except wax-containing or wax-free shellac and/or of different colour index.	There are plenty of variety or tailor made synthetic resins of various properties.
2.	Shellac being natural, is chemically ill-defined, is mixture of several constituent acids, difficult to obtain standard product of assured specifications and quantity every year and price fluctuation is greatest drawback leading consumers to opt for suitable substitute.	Synthetic resins of assured quality and known chemical structure are available. Prices remain stable over years.
3.	Because it is natural it is mixture of many constituents.	Purity is high, more homogeneous.
4.	Due to low melting temperature (65°-75°C), shellac cannot be used for high performance formulations.	Synthetic resins are available with very high melting temperatures (>200°C).
5.	Cannot be tailor-made, suiting a particular characteristics.	Synthetics can be tailor-made suiting the exact demand.
6.	Not soluble in drying oil as such.	Drying oil solubility is an advantage for synthetic resins, products become cheaper.
7.	Cost of shellac is high.	Many general-purpose synthetic resins are cheap, hence finished products are also cheaper.
8.	Its keeping property is different for different crops.	Keeping property, in general, is better, except for some resins, which polymerizes within a few months.

printing ink, polymer and other related industries for the last more than one century. More than 100 applications of shellac have so far been reported by various researchers in scientific journals. Shellac has existed shoulder to shoulder with its synthetic substitutes even after their invention. The growing concern of hazardous nature of synthetic resins, particularly in use in our everyday life, have turned consumers to opt for natural organic-based products, is creating new horizon, new vistas of increased utilization of shellac-based products.

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10

Quality evaluation, standard specification of lac and lac products

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RAW LAC is not of uniform quality, not used as such and is to be subjected to a variety of refining processes to obtain a more purified end product. It is necessary to test the sample for grading and to judge the quality of lac. Further, in the trade a uniform quality is required to be supplied, it becomes necessary to test the sample according to a national standard (BIS Specification) and its acceptability for sustained trade in the country.

Some of the equipments, used in quality evaluation of lac and lac products are: Muffle furnace for ash determination; A.S.T.M. Flow apparatus for flow and life determination; Solvent extraction apparatus for determination of wax; U.V-Visible Spectrophotometer for determination of purity of dye; Melting point apparatus (Electronically operated or Conventional melting point apparatus by using mercury in a crucible) - for determination of softening and melting point; Sand bath with hot alcohol extraction arrangement – for determination of hot alcohol insoluble; and Dubosque colorimeter for determination of bleach index.

Current trade practice

Main criteria for evaluating of stick-lac in trade is *Chowri parta* which is an estimation of the out turn *chowri* or seedlac from 40 kg of stick-lac on the basis of visual examination or actual washing in small lot of representative. As sticklac usually contains various impurities and its quality varies, it is not easy to determine yield of seedlac. Processing centres require services of an expert for purchase of stick-lac. Method of evaluation, however, is open to much improvement. Indian Institute of Natural Resins and Gums has worked out satisfactory method for assaying resin content in sticklac, based on acid value of lac resin, which is accepted in the trade.

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Methods of quality management

Tests which are recommended or actually followed by a number of important official and non–official organizations for trade purpose throughout the world for seedlac and shellac are stated below:

Volatile matter (Moisture): Volatile matter content is determined by heating a weighed specimen of original sample at 41 ± 1°C for 4 hr and then keeping over conc. sulphuric acid (H_2SO_4) in vacuum for 18 hr. Loss in weight (expressed as a percentage) gives volatile matter/moisture present in the sample. In seedlac, volatile matter (%) should not exceed 2.50 % and in shellac it should not exceed 2%.

Hot alcohol insoluble (Impurity test): Matter insoluble in hot alcohol is determined by extracting a known mass of sample with 95% ethyl alcohol ($C_2 H_5 OH$) and determining percentage of un-dissolved residue. This test is essential. In seedlac, impurity ranges from 2 to 5% whereas in hand made and machine made shellac impurity ranges from 0.75 to 3%. However, dewaxed shellac/dewaxed decolourized shellac, impurity should not exceed 0.2 %.

Colour index: It is determined comparing colour of a standard solution of iodine with a solution of the sample in ethyl alcohol by diluting sample solution progressively with alcohol until a close match is obtained. In seedlac, colour index ranges from 8 to 30. In hand made shellac, colour index ranges from 6 to 30 whereas machine made shellac, colour index varies from 8 to 50. In dewaxed shellac, value ranges from 9 to 50 while in dewaxed decolourised shellac it ranges from 0.9 to 5.0.

Flow: Method consists of melting a sample of ground shellac/seedlac (20 mesh/ 40 mesh) in a test tube vertically for 3 min in a thermostatically maintained bath at 100 ± 1°C and tilting the test tube to an angle of 15° for 12 min to permit the sample to flow down the tube and measuring the distance in millimeter. This is an important test and depends upon the agreement between the Buyer and the Seller. Before testing, the sample should be conditioned over saturated solution of sodium dichromate. Average flow of *rangeeni* varieties in 35 to 55 mm and *kusmi* varieties ranges from 60 to 100 mm.

Life (*polymerization time*): Method consists of heating sample of seedlac/ shellac under specified condition in a test tube at 150 ± 1°C and observing the time required for it to attain a rubbery state as indicated by the "spring back" of glass rod when twisted through full circle in molten resin. Before testing, sample should be conditioned in an oven at 41 ± 1°C for 4 hr and finally overnight in a desiccator over conc. sulphuric acid (H_2SO_4). Average life of *rangeeni* varieties ranges from 30 to 50 min and those of *kusmi* varieties ranges from 45 to 70 min.

Bleach Index or *Bleach ability test*: Number of ml of bleach liquor with 3% available chlorine required to bleach 30g of seedlac in sodium carbonate

(Na_2CO_3) is bleach index of seedlac. When all the bleach liquor is consumed, colour of the sample is to be matched with the standard iodine solution in a colorimeter. Actual value is determined following a method developed at this Institute. Amount of bleach liquor added for bleaching is divided into 2 grades and each grade contains two classes.

Grade I : Class A 80 ml and Class B: 100ml.
Grade II: Class A 115 ml and Class B: 140 ml.

Wax: It is a natural constituent of lac resin, varying from about 2.5 to 5.5% depending on the type of lac. There are two methods for determination of wax:

Method I: A specified quantity of sample is dissolved in hot solution of sodium carbonate (Na_2CO_3), wax is separated by filtering, extracted with chloroform and weighed after drying.

Method II: A specified quantity of sample is dissolved in alcohol and wax is separated out at 0°C with the use of filter aid and oxalic acid. Wax is subsequently extracted from filter aid with chloroform and weighed after drying. This method is applicable only in case of dewaxed lac.

Ash: A known weight of sample is heated on a silica or platinum crucible at a low heat, not exceeding dull redness, until free from carbon and then finally heating the crucible in a muffle furnace at a temperature of 650° to 750°C for 4 hr. Amount of ash is computed as a percentage on the lac taken for test. In seedlac, the percentage of ash is agreed between buyer and seller. In hand made shellac, ash percentage ranges from 0.5 to 1.0%. In machine made shellac it should not exceed 0.3%.

Water soluble matter: A known mass of powdered sample is digested with water, made up to a known volume and filtered. Matter that goes into solution is determined by evaporating an aliquot portion of filtrate to constant mass and calculating for the whole solution. In seedlac, it should not exceed 1% and in hand made /machine made shellac, it should not exceed 0.5 %.

Rosin (Detection): Detection and estimation of rosin forms probably the most important item of shellac analysis. When lac is stored for some years, it undergoes a slow process of polymerization as a result of which the flow diminishes appreciably. Hence, to increase flow of old lac, sometimes rosin is mixed with old lac. Presence of rosin in lac can be detected by Halphen Hicks test. It gives a distinct positive indication even with samples containing 0.1% rosin and therefore, adopted as a standard test practically in all recognized institutions doing lac analysis. Percentage of rosin can be calculated from Iodine value. The test is compulsory and essential for shellac.

Orpiment (Detection): Presence of 0.5% of orpiment in a sample of shellac gives shellac flake a yellow, opaque appearance. Even a trace of orpiment can be detected from a solution in spirit or in aqueous borax, if shellac is free from dirt.

Acid value: Number of mg of KOH required to neutralize free acid present in 1g of lac sample is acid value of the sample. An alcoholic solution of sample is titrated with a solution of potassium hydroxide (KOH) solution required to neutralize free acid present in 1 g of sample of lac with the help of thymol blue as indicator. Acid value of lac ranges from 65 to 75.

Iodine value: A known weighed sample is taken in an iodine flask and dissolved in a known volume of glacial acetic acid by slightly warming on water bath at a temperature of 65°–70°C. A known volume of chloroform is then added and solution is cooled to room temperature. A blank test without sample is also run concurrently. A known volume of Wijs solution is added in both flasks and kept in water bath at a temperature of 20° to 22°C for 1 hr. After 1 hr, a known volume of 10% Potassium iodide (KI) solution is added in both the flasks and titrated against N/10 sodium thiosulphate solution using starch as indicator. Iodine value is calculated by usual method. Iodine number is the number of grams of iodine absorbed by lac expressed as a percentage. Iodine value of lac ranges from 14 to18, if it is more than 18, sample should be tested for rosin.

Estimation of rosin

Percentage of rosin in shellac shall be determined from the following formula:

$$\text{Per cent of rosin} = \frac{(X-8)}{228-18} \times 100$$

where, X, Iodine value of mixture (sample); Iodine value of shellac, 18; Iodine value of rosin = 228.

Saponification value

A known weight of substance is dissolved in known volume of N/2 alc. KOH and the solution is refluxed on a water bath for 3 to 4 hr. A blank test with known volume of N/2 alc. KOH only is also run concurrently. Both solutions are then titrated against N/2 HCl using thymol blue as external indicator. Number of mg of KOH required for complete saponification of 1 g of lac is saponification value of lac. Saponification value of lac ranges from 220 to 230.

Hydroxyl value

A known weight of sample taken in a flask fitted with an air condenser, which is heated in oil bath, with known volume of acetylation mixture at 100° to 105°C for 1 hr. A blank test with only known volume of acetylation mixture is also run concurrently. The 20 ml of hot distilled water is poured down the condenser and heating is continued for 15 min, after which flask is cooled and 50 ml of a mixture of benzene (C_6H_6) and butanol (1:2) is poured down the condenser. Condenser is then removed and contents of the flask are titrated with 0.5N alcoholic KOH solution using phenolphthalein as indicator. Number of milligram of KOH necessary to neutralize acetic acid liberated by hydrolysis of acetyl derivatives of 1g of material is hydroxyl value of the sample. Hydroxyl value of lac ranges from 250 to 280.

Carbonyl value

Acid value of the sample is first determined; 0.5 g of sample is dissolved in 20 ml alcohol and to this solution 5 ml of distilled water, 20 ml sodium suphite solution (0.8 N) and 5 ml of 0.1 N sulphuric acid (H_2SO_4) are added. These are thoroughly mixed and kept aside for 5 min. Then it is titrated against 0.1 N NaOH solution. A blank test is also run concurrently with the above reagent except lac and the value is calculated from the following formula:

$$\text{Carbonyl value} = A - [(V_1 - V_2) \text{ X } N \text{ x } 40 / W]$$

where, A, acid value of the substance; V_1, volume of NaOH required to neutralize the sample; V_2, volume of NaOH required to neutralize the blank; N, normality of NaOH solution; and W,= weight of sample taken in g. Carbonyl value of lac ranges from 7.8 to 27.5.

SEEDLAC – SPECIFICATION

The usual trade description of seedlac is based on Indian names of host trees, crop season, visual differences or a combination of these. Use of these grade designations led to confusion and some marketing difficulties. A new system was adopted in the national and international standard so that seedlac can now be completely identified by a combination of BIS grade and trade grade. There are 5 grades of seedlac: (*i*) special, (*ii*) grade A, (*iii*) grade B, (*iv*) grade C, and (*v*) grade D.

For matter insoluble in hot alcohol, two limits are prescribed in line with trade practice: a basic limit and a relaxed limit. Relaxed limit shall be the limit for rejection.

Requirement for non-volatile matter soluble in cold alcohol has not been retained, as this requirement is applied in practice for waste products of lac only.

One of the requirements for seedlac namely, matter insoluble in hot alcohol, is included in this national standard as an essential clause.

The remainders are optional namely, colour index, volatile matter, bleach index, particle size, matter soluble in water, wax and ash.

Scope and field of application

National standard specifies requirements and methods of test for seedlac.

National standard is intended chiefly to cover technical provisions for guiding purchase of material but does not include all the necessary provisions of a contract.

Definitions

For the purpose of this national standard the following definitions apply:

Sticklac: Raw material, the natural product of lac insect.

Seedlac: Semi-refined product obtained by washing crushed sticklac.

Approved sample: Sample agreed upon between Purchaser and Vendor as standard for colour and appearance.

Form and condition

Form and condition of seedlac are subjected to agreement between Purchaser and Supplier.

Grades

Five grades of seedlac namely, special, A, B, C, D and E are specified. Further, if required by purchaser, names of the grades as prevalent in trade (Table 10.1).

Table 10.1. Correspondence between National Grade and Trade Grade

National Grade	Trade Grade
Special	Golden *kusmi* seedlac/Golden Bysakhi seedlac and grade I, class A seedlac
A	*Kusmi* one seedlac/Grade II, class A seedlac
B	Manbhum fine Bysakhi seedlac/Grade I, class B seedlac
C	Fine Bysakhi seedlac/Grade II, class B seedlac
D	Genuine Bysakhi seedlac

Mandatory requirements

Matter insoluble in hot alcohol: Seedlac shall not contain more than the basic limits of matter insoluble in hot alcohol specified in Table 10.2, when determined by either of the methods described in the processes, as agreed between Purchaser and Supplier. By agreement between Purchaser and Supplier, basic limit may be relaxed but it shall not in any case exceed relaxed limit, Table 10.2.

Table 10.2. Basic and relaxed limits of hot alcohol insoluble

Grade	Basic limit %	Relaxed limit %
Special	2.0	3.0
A	3.0	4.0
B	3.0	4.0
C	3.0	5.0
D	5.0	7.0

Optional requirements

Volatile matter: Seedlac shall not contain more than 2.5% of volatile matter (moisture) as determined by the method adopted in laboratory.

Bleach index: Bleach index of seedlac shall be determined by the bleachability test. It shall be carried out, if agreed between purchaser and supplier in accordance with process adopted in laboratory.

Colour index: Colour index of seedlac, as determined by the method shall not exceed the limits given in Table 10.3.

Table 10.3. Limits of colour index of seedlac

Grade	Colour Index
Special	8
A	10
B	12
C	18
D	30

Alternatively, appearance and colour of seedlac shall not be inferior to those of an approved sample when judged by visual examination.

Matter soluble in water: Seedlac shall not contain more than 1% of matter soluble in water and aqueous extract shall be neutral to methyl red. Matter soluble in water shall be determined by the method adopted in laboratory.

Ash: Limits and methods of test for ash content of seedlac shall be subject to agreement between Purchaser and Supplier.

Wax: Seedlac shall not contain more than 5.5% of wax when determined by the method adopted in laboratory.

Particle size: Not more than 20% passing through 600 μ (micron) IS Sieve and not more than 5% through 425 micron IS Sieve.

Flow: This test is subject to agreement between Buyer and Seller.

SHELLAC -SPECIFICATION

The specification covers for both hand made as well as machine made shellac and has been divided into two parts one for hand made shellac and another for machine made shellac.

HAND MADE SHELLAC

In the beginning of the trade, grading of hand made shellac was based on Indian names of host trees, crop season, visual differences or a combination of any of these. Use of these grade designations has led to confusion and some marketing difficulties. In 1957, it was decided to adopt only 6 grades of hand made shellac, which were independent of names of host trees and seasons. However, expectation that specification for hand made shellac would be increasingly adopted in trade and ultimately replace traditional grade designation did not happen. A new system was, therefore, adopted in the national/international standard so that Hand Made Shellac can now be completely identified by combination of national/international grades and trade grade. For matter insoluble in hot alcohol, two limits are prescribed, in line with the trade practice, a basic limit and a relaxed limit which shall be the limit for rejection.

Requirements

Matter insoluble in hot alcohol, Colour Index and Absence of rosin and orpiment are included in this national standard as essential clauses. The remaining requirements are optional: Volatile matter (moisture); Wax; Ash; Matter soluble in water; Flow; Heat polymerization time (Life); Acid value; Lead content and Iodine value.

For purpose of deciding whether a particular requirement of this National Standard is complied with, the final value, observed or calculated, expressing the result of a test or an analysis, shall be rounded off to the same number of places as specified value, it being always understood that analyst will carry out determination to at least one place more than in specified value.

Scope and field of application

National standard specifies requirements and corresponding methods of test for hand made shellac. The standard is intended chiefly to cover technical provision for guidance in purchase of the material, but does not include all necessary provision of a contract.

Definitions

For the purpose of the National Standard, the following definitions apply:

Stick-lac: The raw material, natural product of lac insects.

Seedlac: Semi-refined product obtained by washing crushed stick-lac.

Shellac: Product obtained by refining seedlac by heat process or by solvent process or by both heat and solvent processes.

Approved sample: Sample agreed upon between purchaser and supplier as standard for colour and appearance.

Form and condition: Handmade shellac shall be as flake, sheet button or in any other form agreed between purchaser and supplier.

Grades

The grades (61) of Handmade shellac are specified as Special, A, B, C, D and E. Further, if required by purchaser name of grades as prevalent in trade shall be indicated in addition in parentheses:
Grade Special (Golden *kusmi*), Grade B (Lemon No. 2) Table 10.4.

Matter insoluble in hot alcohol: Handmade shellac shall not contain

Table 10.4. Correspondence between National Grade and Trade Grade

National Grade	Trade Grade
Grade special	Superior *kusmi* button lac, Special *kusmi* lemon shellac
Grade A	Lemon I shellac, Pure I button lac, Light pure button lac, Superior Lemon shellac, Golden shellac
Grade B	Lemon II Shellac
Grade C	Super fine shellac, standard I shellac, yellow orange shellac
Grade D	Pure TN shellac
Grade E	I TN shellac.

matter insoluble in hot alcohol, determined by either of prescribed methods as agreed between purchaser and supplier in excess of limits (Table 10.5). Basic limit may be relaxed by agreement between purchaser and supplier, but it shall not exceed in any case relaxed limits of Table 10.5.

Table 10.5. Requirements of matter insoluble in hot alcohol different grades of shellac

Grade	Basic Limit (%)	Relaxed limit (%)
Special	0.75	1.00
A	1.00	1.50
B	1.25	2.00
C	1.50	2.50
D	2.50	3.50
E	3.00	5.00

Rosin: Handmade shellac shall not contain any rosin when tested by the prescribed method.

Orpiment: Handmade shellac shall not contain any orpiment when tested by the prescribed method.

Optional requirements: The optional requirements given below shall be subject to agreement between Purchaser and Supplier.

Volatile matter: Handmade shellac shall not contain more than 2% volatile matter, as determined by prescribed method.

Colour index or colour and appearance: Colour index of hand

Table 10.6. Requirement regarding colour index of different grades

Grade	Colour Index
Special	6
A	12
B	15
C	18
D	25
E	30

made shellac as determined by the prescribed method shall not exceed limits give in Table 10.6.

Alternatively, the appearance and colour of shellac shall not be inferior to those of an approved sample when judged by visual examination.

Wax: Hand made shellac shall not contain more than 5.5% wax when tested by prescribed method.

Table 10.7. Limits of ash content of different grades of shellac

Grade	Colour Index
Special	0.50
A	0.50
B	0.50
C	1.00
D	1.00
E	1.00

Ash: Hand made shellac shall not leave, on incineration, ash in excess of limits given in Table 10.7 when tested by prescribed method.

Matter soluble in water: Handmade shellac shall not contain more than 0.5% of matter soluble in water and aqueous extract shall not be acidic to methyl red or alkaline to bromothymol blue. Matter soluble in water shall be determined by prescribed method.

Flow test: Handmade shellac shall have a flow within range agreed to between Purchaser and Supplier, when tested by prescribed method.

Heat polymerization test: Handmade shellac shall have heat polymerization time within range agreed to between Purchaser and Supplier when tested by prescribed method unless otherwise agreed to; and temperature of test shall be 150 ± 1°C.

Acid value: Acid value of hand made shellac shall be fixed, while tested by method prescribed in the book, if desired by agreement between purchaser and supplier.

Lead content: Maximum limit for lead content shall be subjected to agreement between Purchaser and Supplier and lead content shall be determined by prescribed method.

Iodine value: Maximum limit to Iodine value shall be as agreed to between purchaser and supplier when determined by prescribed method.

MACHINE MADE SHELLAC

Machine made shellac has been divided into four main types: (*i*) on the basis of the method of manufacture, (*ii*) into grades, (*iii*) within each type, and (*iv*) on the basis of colour. Requirements for matter insoluble in hot alcohol, colour index and ash have now been prescribed based on the new system of types and grades.

Like handmade shellac, machine made shellac also requires three essential tests: Matter soluble in hot alcohol, Colour index and absence of rosin and orpiment. The remaining requirements are optional: (a) volatile matter, (b) wax, (c) ash, (d) matter soluble in water, (e) Flow, (f) Heat polymerization test, (g) acid value, (h) lead content, (i) iodine value, and (j) clarity of solution. Scope and field of application, definition, form and condition are same as in hand made shellac.

Types and Grades

Four types of machine made shellac are specified namely:

Type I	Produced by heat process
Type II	Produced by hot solvent process
Type III	Dewaxed shellac
Type IV	Dewaxed and decolourised shellac.

Five grades in each of Types I and II namely, grades IA, IB, IC, ID, IE, IIA, IIB, IIC, IID and IIE are specified. Four grades in each of Types III, and IV namely, grades IIIA, IIIB, IIIC, IIID, and IVA, IVB, IVC, IVD are specified.

Mandatory requirements

Matter insoluble in hot alcohol: Machine made shellac shall not contain matter insoluble in hot alcohol determined by either of the method specified, as agreed to between Purchaser and Supplier, in excess of limits given in Table 10.8.

Table 10.8. Maximum limits for mater insoluble in hot alcohol

Type	Maximum
I	0.75
II	0.3
III	0.2
IV	0.2

Colour index and Colour appearance: Colour index of machine made shellac, as determined by prescribed method, shall not exceed limits given in Table 10.9.

Table 10.9. Limits of colour index of different grades

Grade/type	A	B	C	D	E
I, II	8	12	22	35	50
III	9	20	35	50	-
IV	0.9	2.0	3.5	5.0	-

Alternatively, the appearance and colour of shellac shall be not inferior to those of approved samples when judged by visual examination.

Rosin: Machine made shellac shall not contain any rosin when tested by the prescribed method.

Orpiment: Machine made shellac shall not contain any orpiment when tested by prescribed method.

Optional requirements

Volatile matter (moisture): Machine made shellac shall not contain more than 2% volatile matter or moisture as determined by prescribed method.

Wax: Machine made shellac of Type I and Type II shall not contain more than 5.5% wax, and that of Type III and Type IV not more than 0.2% of wax when tested in accordance with methods I and II respectively, as specified in prescribed method.

Ash: Machine made shellac shall not contain more than 0.3% of ash when tested by prescribed method.

Matter soluble in water: Machine made shellac shall not contain more than 0.5% of matter soluble in water and aqueous extract shall not be acidic to methyl red or alkaline to bromothymol blue. Matter soluble in water shall be determined by prescribed method.

Flow: Machine made shellac shall have a flow within the range agreed to between Purchaser and Supplier when determined by prescribed method.

Heat polymerization time: Machine made shellac shall have a heat of polymerization time within range agreed to between Purchaser and Supplier when tested by method specified.

Acid value: Acid value of machine made shellac shall be fixed, as desired by agreement between Purchaser and Supplier. It shall be determined by the method specified.

Lead content: Maximum limit for lead content shall be subjected to agreement between Purchaser and Supplier and lead content shall be determined by the specified method.

Iodine value: Maximum limit for iodine value shall be as agreed to between Purchaser and Supplier, if required it shall be determined by the prescribed process.

Clarity of solution: This requirement is applicable to Type III and Type IV and shall be subjected to agreement between Purchaser and Supplier. Shellac shall show no turbidity, when tested by the specified method.

BLEACHED LAC: SPECIFICATION

This national standard covers bone-dry bleached lac, an intermediate-surface dry (air dry) bleached lac, and wet bleached lac. The 3 differ in their requirements in the moisture content. No distinction is sought to be introduced between bone dry, klin-dry bleached lac or between various designations of intermediate type covering dried, crushed hanks or flats in granules or flakes or between wet bleached lac in hand, bar or any other form. Only three conditions, *i.e.*, (*i*) bone dry, (*ii*) surface dry and (*iii*) wet; and two types in each condition namely, (a) regular bleached lac (cloudy or waxy), and (b) refined bleached lac (transparent or wax-free), more briefly indicated as "regular and refined" are recognized.

(*i*) No limit has been specified for chlorine content of bleached lac. Normally, chlorine content of bleached lac varies between 1.5 and 4.5% in moisture free material but it is desirable to maintain it at a low value (at 3% maximum).

(*ii*) Like wise, no limit has been specified for acid value of bleached lac. This depends upon the methods of bleaching. Acid value of good bleached lac normally ranges from 73 to 93 for moisture free material.

(*iii*) Similarly, mineral acid content of bleached lac should also be as low as possible equivalent to 0.4% of mineral acid.

(*iv*) Maximum limit for volatile matter (moisture) in bone-dry material has been specified as a mandatory requirement, *i.e.,* a maximum of 6%. In so far as surface dry (air- dry) and wet-bleached lacs are concerned, actual limits have been made the subject of agreement between purchaser and vendor. Normal moisture content of the surface dry material does not exceed 12% and that of wet bleached lac does not exceed 30%.

Scope and field of application

(*i*) This standard specified requirements and methods of test for bleached lac in any form that may be agreed between purchaser and vendor.

(*ii*) This standard is intended chiefly to cover technical provisions for guiding purchase of material but does not include all necessary provisions of a contract.

(*iii*) Limits specified in this standard are not to be exceeded.

Definitions

For the purpose of this standard, the following definitions apply:

Stick-lac: The raw material, natural product of lac insect.

Seedlac: Semi-refined product obtained by washing crushed stick lac

Shellac: Product obtained by refining seedlac, by heat process or by solvent process or by both heat and solvent process.

Bleached lac

(*i*) *The product obtained by subjecting seedlac or shellac:* These products are placed in solution to a process of bleaching and then recovering the product in solid form.

(*ii*) *Regular (cloudy and waxy) bleached lac:* Ordinary type of bleached lac from which wax has not been removed.

(*iii*) *Refined (transparent or wax free) bleached lac:* This type of bleached lac from which wax has been removed during the process of manufacture.

Approved sample: Sample agreed upon between Purchaser and Vendor as standard for colour and appearance.

Form: The form of bleached lac is subjected to agreement between Purchaser and Vendor.

Condition and Type: Three conditions of bleached lac are specified: (*i*) Bone-dry, (*ii*) Surface dry, and (*iii*) Wet. Two types are specified for each of these conditions namely, regular (cloudy and waxy), refined (transparent and wax free).

Mandatory requirements

Volatile matter (moisture): Bone-dry bleached lac shall contain not more than 6% of volatile matter as determined by prescribed method. Percentage of volatile matter present in surface dry bleached lac shall be subject to agreement between Purchase and Vendor and shall be determined by prescribed method.

Matter insoluble in Hot-alcohol: Bleached lac shall not contain matter insoluble in hot-alcohol, computed on the basis of moisture free materials in excess of the limits given below:

Regular 1.1%, refined 0.2%. Matter insoluble in hot-alcohol shall be determined by either of the methods prescribed in the process.

Colour: Appearance and colour of bleached lac shall not be inferior to that of the approved samples when judged by visual examination. Alternatively, colour in solution may be tested by either of method described in the process, as agreed upon between purchaser and vendor. However, colour index of bleached lac ranges from 0.3 to 1.5.

Wax: Refined bleached lac shall not contain wax, as determined by appropriate method described in the process. Regular bleached lac contains wax not more than 5.5% when tested by the prescribed method [regular 5.5%, refined 0.2%].

Ash: Bleached lac shall not leave ash, as determined by the described process and computed on the basis of moisture free material, in excess of the limits given as: Regular 1.0%, and refined 0.5%.

Rosin and copals: Bleached lac shall contain no rosin, as tested by the prescribed method. Bleached lac shall not contain any copal when tested by the prescribed process.

Matter soluble in water: Bleached lac shall not contain matter soluble in water as determined by the prescribed process and computed on the basis of moisture free material in excess of the limits given: Regular 1%, refine 0.30%.

Optional requirements

Total chlorine: Chlorine content of bleached lac is subjected to agreement between Purchaser and Vendor and shall be determined by the process prescribed.

Acid value and mineral acid: Acid value of the material is subjected to agreement between Purchaser and Vendor and shall be determined by prescribed process. Mineral acid content of bleached lac is subjected to agreement between Purchaser and Vendor and shall be determined by the prescribed process.

Free chlorine: A requirement for the absence of free chlorine shall be subjected to agreement between Purchaser and Vendor, when specified; aqueous extract of the material shall not show presence of free chlorine when tested by the prescribed method.

Arsenic: Arsenic content of bleached lac is subjected to agreement between Purchaser and Vendor and when tested by the prescribed process.

Lead: Lead content of bleached lac is subjected to agreement between Purchaser and Vendor and shall be determined by the prescribed method.

Specifications of a few commonly used shellac based products are enumerated here.

1. ***Specification for shellac varnish***

Characteristics	Requirement
Drying time, Max^{m}.(Hard Dry)	2 hr
Finish	Smooth, glossy
Ash content % by wt. (Max^{m})	0.50
Freedom from Rosin	Shall no positive reaction when subjected to Halphen-Hicks test

Source: (IS:347–1975)

2. ***Specification for french polish***

Characteristics	Requirement
Drying time (hard dry)	Not more than 2 hr
Finish	Smooth and glossy
Ash content % by wt. (Max^{m})	0.50
Iodine value Max^{m}	20.0
Colour Index	Shall not exceed 18
Matter insoluble in hot alcohol of the residue % by wt. Max^{m}	0.50
Keeping properties	Not less than 1 year from the date of manufacture

Source: (IS: 348–1968)

3. ***Specification for shellac wax***

Characteristics	Requirement Grade I	Requirement Grade II
Relative density at 27°C	0.960 to 0.995	0.965 to 0.990
Melting point °C	83 to 84	75 to 85
Acid value	14 to 22	12 to 25
Saponification value	82 to 95	-
Iodine value Max^m	10	10
Resin content (Matter soluble in 70% ethanol)	5	-
Volatile matter, percent by weight Max^m	1	-
Ash, Per cent by weight	0.2	1.0

Source: (IS: 5467–1969)

4. ***Specification for sealing wax (First Revision) IS 868: 1990***

Grades: Three shall be 2 grades of sealing wax:

(a) Grade I: A grade of sealing wax to give satisfactory adhesion to hard and medium-sized papers. It shall have two types: Type 1: With shellac not less than, 36%, and Type 2: May or may not contain shellac.

(b) Grade 2: Low grade sealing wax to be used on all types of paper other than those mentioned above on material other than paper and glazed tag labels.

Requirements: Sealing wax shall consist of ingredients which are non-injurious to health and do not harm surfaces on which they are used. The common ingredients for making sealing wax are shellac, rosin, mineral fillers and pitch.

For Grade I, Type I of sealing wax: The minimum shellac content shall be 36%.

For Grade 2, of sealing wax: Shellac content and pitch content should be minimum 10% and 30%, respectively. Mineral loading should be within the limits of 30 to 40% for grade I and 40 to 50% for grade 2 of sealing wax.

Colour: Sealing wax shall be uniform in colour.

Odour and Fuming: Sealing wax when melted or burnt shall not fume noticeably or give off an offensive odour.

Adhesion to surface: Sealing wax shall be capable of adhesion to the appropriate surfaces, according to grade, when tested by the method specified.

(a) *Grade I:* Heavy weight hard surfaced kraft, bond and sulfite papers and medium sized kraft paper.

(b) *Grade II:* Surfaces other than those of hard and medium finished papers including glazed, tag labels hessian and cloth.

Capability of taking impression: All grades of sealing wax shall be capable of taking a clear impression of the die with fine inscriptions when tested by the method.

Heat resistance: The test is carried out by heating the seals affected on a glass plate or paper for 5 hr in hot oven at 55 ± 0.5°C for grade I and at 60 ± 0.5°C for grade II.

Resistance to heat polymerization: Sealing wax of both grade I and grade II are tested at 130 ± 5°C for 2.5 hr. The material shall be taken to have satisfied requirement of the test, if at the end of 2.5 hr the sealing wax does not turn spongy or rubbery or become infusible.

5. ***Specification for byproduct of lac (IS: 2978-1986)***

Types: There are following types of by-products of lac:

Molamma Spl ; *Molamma* I ; *Passwa* ; *Kiri* I ; *Kiri* II ; *Kiri* III

Particle size: 80% minimum, Molamma spl: Passing through 600 micron IS sieve (IS: 460 (part I) 1978

Molamma I: 80% minimum, passing through 600 micron IS sieve.

There shall be no particle size limitation in the case of Passwa, Kiri I, Kiri II and Kiri III.

Lac content: Molamma, Passewa and *Kiri* shall contain lac as given here.

Material	Lac content	Per cent Max^{m}
Molamma Spl	80.0	85.0
Molamma I	70.0	Below 80.0
Passewa	70.0	No limit
Kiri I	55.0	65.0
Kiri II	40.0	Below 55.0
Kiri III	30.0	Below 40.0

Colour Index: For Molamma and Passewa shall be agreed between Buyer and Seller.

Kiri – No limit of colour index.

6. ***Specification for Aleuritic Acid***

Characteristics	Requirements
Moisture, per cent by Mass, Max	1.0
Molecular Mass (from Acid value)	303-308
Melting Point (°C)	96
Relative density 27±2°C and 65 ± 5% R H	1.1
Infrared spectrum	Close match to the approved sample

Source: (IS:13160-1991)

7. *Specification for Lac dye*

Characteristics	Requirements
Melting point	Above 230°C with charring
Volatile Matter at 135°C present by Mass	0.1
Acid Value	234-245
Ash content	0.7% Max
Insoluble matter %by mass	
(a) Cold water	52
(b) Hot water	101.0
(c) Hot alcohol	
Dye content % by mass	90
UV-Visible Absorption spectrum, *max*	230, 292, 340, 500 and 530 nm
Lead mg /kg max.	10
Arsenic mg/kg	3

Source: (IS: 12921-1990)

8. *Specification for Shellac Jointing Compound/Gasket Shellac Compound*

Characteristics	Requirements
Total solids	Not less than 60 %
Drying times	Tack free drying with 20 min.
Acid value	Not more than 50

Source: (IS:3447- 1993) (First Revision)

Note: Requirements for resistance to motor gasoline and resistance to lubricating oils are deleted as these are found to be redundant, in the present context.

9. *Indian Standards of lac and Lac products*

Specification No.	Titles
IS: 15-1973	Seedlac: specification (second revision)
IS:16 (Part 1)-1991	Shellac: specification Part 1 (Hand made shellac) (Third revision)
IS:16 (Part 2)-1991	Shellac: specification Part 2 (Machine made shellac) (Third revision)
IS: 17- 1973	Bleached lac: Specification (Second revision) Amendment 2
IS: 6921- 1973	Methods of sampling and test for lac and lac products
IS: 2978- 1986	By products of lac (First revision)
IS: 348- 1968	Requirement of French polish
IS: 868- 1990	Specification for sealing wax
IS: 347-1975	Requirement of varnish (shellac)
IS: 13160- 1991	Aleuritic acid: specification
IS: 12921-1990	Lac dye: specification
IS: 5467- 1986	Shellac wax (First revision)
IS: 12518- 1988	Shellac bond powder
IS: 4908- 1968	Gloosary of terms used in lac industry
IS: 3447- 1993	Shellac jointing compound
IS: 6921- 1989	Amendment No.1, Alternative method of determination of colour index

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Future scope of use of shellac

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'GREEN CHEMISTRY' also known as sustainable chemistry, is an umbrella concept, which is gaining momentum after formation of the Environmental Protection Agency and celebration of first Earth Day in 1970 (Prasad, 2006). By definition, Green chemistry is design, development, and implementation of chemical products and processes to reduce or eliminate use and generation of substances hazardous to human health and environment (Prasad, 2006). Consumers have become conscious about the evils of synthetics. In 2001 around 20,300 tonnes of plastic packaging waste was recycled (equal to present lac production in India), up 13% from 2000. Very high goals have been set for 2016 A D. Here lies strength of biodegradable natural resin lac over synthetics in the vast world of polymeric materials, its chance to sustain challenges from its substitutes, warrants wisdom applied for design of environment-benign products/ processes to maximize use of natural resin in products where it has been replaced by the synthetics.

Growing concern of the menace of non-destroyable synthetics, have compelled intellectuals in the look out of safer natural substitute. In this changed scenario, there is a need for strategic planning, identify key issues to be addressed to put shellac on the saddle of fast changing consumer world. At the first place, strengths of shellac is to be clearly understood; products/processes in select areas are to be chosen; requirements to be fulfilled; efforts to be made for mass awareness and aggressive marketing. Few fields in which lac and lac-based products possess potential for application are described here.

Fruits and vegetables coating

India produces annually about 150 million tonnes of fruits and vegetables. Installed capacity of fruits and vegetables processing industry has increased from 1.108 million tonnes in January 1993 to 2.118 million tonnes in January 2006 (web site indiainbusiness.nic.in). Processing level of fruits and vegetables is, however, very low, estimated around only 2.20%

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of total production. Total export for processed fruits and vegetables in 2004-05 was of Rs 14627.2 millions. Food processing industry is one of the largest industries in India. It is ranked fifth in terms of production, consumption, export and expected growth (web site sethaassociates.com). It is projected that market for Asian Food Processing sector, currently valued at US $400 millions, it is likely to proliferate rapidly @12 to 15% per annum for the next 5 years (web site indiainbusiness.nic.in). India is projected to remain as a net exporter of fruits and vegetables. In Europe and USA, shellac wax is used for coating fruits (citrus, apples etc.) and vegetables; unfortunately, such a huge maiden field of application is yet to take a desired entrepreneurship in India. Under the circumstances, lac-based coating formulation is likely to have a potentially viable market as a coating material for fruits and vegetables for extending post-harvest life. A few coating compositions were developed at this Institute for extending post-harvest life of certain fruits and vegetables, rigorous evaluation is under process. Effort is to be continued to formulate suitable high performance coating compositions for use in this highly potential application field, as a few coating composition based on natural material are already in use.

Soft drinks

Our country exported Rs 1,140 millions worth alcoholic and non-alcoholic beverages in 2004-05 (web site indiainbusiness.nic.in). There is a report that China is already using lac dye in soft drink formulations. The Food Additive Hygiene Standards of China approves use of lac dye (code no. 08.104) as a colouring agent in fruit/vegetable drinks, carbonated drinks, blended wines, candies, fruit *jams*, condiments and sauces, with a maximum permissible dosage of 0.5g/kg body weight (web site of Shefexil). This use is yet to start in our country, an appreciable scope of use is awaited for food grade lac dye in this sector. Soft drink bottling is expected one of the most promising sub-sectors in coming years.

Chocolate and candy coating

Shellac is used for coating of chocolates and candies for preservation and protection from moisture. The income potential of manufacture of chocolate and candy is literally unlimited. It is projected that Online candy store can expect to earn anywhere from $5,000 to $25,000 per month, Brick-and-mortar shop can expect to earn $15,000 and up, Self-serve candy shop can earn $20,000 per month or more, Gift basket business can earn $7,500 or more per month,and chocolate retail is a $19 billion market, and candy is a $9 billion market world wide.

Demand for chocolate and candy is increasing by 3.5% annually. As people are getting more aware about antioxidant health benefits of chocolate, it is expected that customers asking for this kind of more organic products. Code no. of shellac under the Australia and New Zealand Food Standards Council is 904 /E904@ ("@" denoting that the product is of animal origin), as a food additive used as a glazing agent, in chocolates, confectionery, fizzy drinks, medications etc (web site of Shefexil). The Food Additive Hygiene Standards of China approves shellac (code no. 14.001) for use as a coating agent in the manufacture of chocolates and waffles with a maximum dosage of 0.20 g/kg body weight (web site of Shefexil). Under the circumstances, quality of dewaxed shellac is to be ensured for steady supply. Researches are needed on reduction in cost of dewaxed lac for sustained utilization in this sector.

Pharmaceutical glaze

Shellac (dewaxed decolourised) is being used as pharmaceutical glaze for tablets and pills since long, although some alternative coating materials are also used presently, but its natural origin might give an edge over animal by-product gelatin. Uninterrupted supply of quality dewaxed decolourised shellac must be ensured in order to sustained share of a sizeable export market.

Paints and dye

This petro-chemical sector has been growing @14 to 15% in India. Total market size is Rs 46 billions and growth rate is 12% per annum though per caput consumption is very low (400 g) in India than developed countries like USA (15 kg). Rigorous efforts may be made for promotion of lac-based varnish, paint and lac dye in this sector. Even if a fraction of the potential consumption is realized, this will lead to an increase in consumption of shellac and dye. The shellac has excellent compatibility with acrylic resin and can be used in water thinnable interior decorative paint formulations. More study is to be made for promotion of this kind of product.

Electronic components

Printed circuit board assembly and original design manufacturing are set to grow to $2.5 billions by 2010 A D (web site theindusview.com). This is because of increasing demand for telecom equipment like mobile handsets. Global electronics manufacturing service providers like Flextronics International, Jabil Circuits, Elcoteq SE and Soleqtron are expected to establish manufacturing bases in India (web site of theindusview.com). Hon Hai Precision Industry, the largest manufacturer of connectors for use in PCs in Taiwan and San Jose, California headquartered, Sanmina-SCI leading electronic manufacturing service provider Sanmina-SCI are in the process of setting up their units. Jabil Circuits has plans to invest up to $100 millions in India over next few years (web site of theindusview.com). Domestic companies like TVS

Electronics, Chennai-based computer peripherals manufacturer are also expanding their operations (web site of theindusview.com).

AT and S, Europe and India's largest producer of printed circuit boards and one of the world's most successful suppliers to the mobile phone industry, posted sales of EUR 375 m in 2005/06, a 13% increase. Operating profit (EBIT) for the year was up 24%, to about EUR 26 m (web site emsnow.com). There is an ample scope to promote shellac-based insulating coating formulations in this sector.

Blend of shellac with different polymers

From IXth plan to Xth plan period, there has been 84.3% increase (4118 kt to 7591 kt) in the consumption of different polymers/polymeric products in India, which is 380-time lac produced in the country. The consumption in the coming years is expected to be more. Researches revealed that shellac is compatible with a number of synthetic resins/polymers. The possibility of utilization of shellac polymer blends, so that shellac can find application in this fast developing polymer sector, in which even a small percentage of use of shellac will ultimately result in a new avenue for substantial consumption of shellac, where further study is needed.

Cost of shellac has increased considerably (almost doubled in the last 5-6 years). Making the situation worse, the costs of common solvents (commercial grade) of shellac have also increased considerably in the last 6 years. The rise noted in the prices is as follows: n-butanol 52%, isopropyl alcohol 40%, toluene 107% and xylene 106%. Under the situation, costs of the shellac-based varnishes are bound to become costlier, making products less competitive. Since costs of the solvents are guided by the petroleum prices, which are bound to see such adversaries, cost of shellac has to be brought down to sustain trade for a longer period. Interestingly, costs of natural gums (which are also forest collections and mostly exported like lac), did not experience such violent price fluctuations; the rise in the prices of a few gums in the last 6 years are rosin 14%, benzoin 3.9%, *ghatti* 14%, *guar* 16% and *karaya* 7%. The reason for high prices of raw lac compared to raw natural gums, is difficult to understand.

Shellac and other natural resin/gum combination

Since some of the natural resins and gums produced in the country possess very well coating and film forming properties, possessing diverse application potential like shellac. Export of *guar* gum in 2004-05 was more than Rs 6,640 millions (web site indiainbusiness). Researches are needed to explore possibility to design and develop products based on shellac and other natural resins/gums. Since costs of most of gums/resins are less than that of shellac, the reaction product is expected to yield different kind of commercially viable utility products.

Shellac-based formulation in solid form

Since no solvent is totally safe, researches may be made to develop compositions using shellac in the solid form, *e.g.*, hot melt adhesive, shellac based moulding powder, shellac based powder coating composition etc.

Shellac-drying oil combinations

Shellac goes into drying oils in presence of catalysts and accelerators at high temperature. Shellac-drying oil combination products, developed earlier, are required to be examined further for promotion in the market in view of the recent price hike of solvents.

Some other possible fields of applications in the coming years are enumerated here:

1. *Packaging:* Coating of packaging materials of food items.
2. *Pharmaceuticals:* Coating of tablets, food grade lac dye for colouring tablets, syrups.
3. *Electronics:* Finishing and protective varnish for coating of PCB, electronic components.
4. *Education:* Coatings on maps and blackboards.
5. *Telecommunication:* Finishing and protective coatings for electronic components.
6. *Consumer products:* Varnishes for furniture, emulsion paint, blends with compatible polymers.
7. *Strategic applications:* Coating of ammunitions, rifle butts.
8. *Agriculture:* Slow release fertilizer.

Strategies to maintain global leadership in processing, product development

World population has reached 6.5 billion, as on Saturday 24 February 2006, it is expected to reach 7.3 billion in 2016 A D. All industries make a prior planning to set a target for meeting future demand. For example, demand for cast polymer in the USA is forecast to advance 4.1% per annum, reaching 1.2 million tonnes in 2010 A D. It is not known whether there is any projection of possible demand of lac in the next 10 years. At present, taking into account India's annual production figure of 20 kt, India produces 3 g of lac per person of world population. Considering India's present population as 1,100 million, consumption of lac is 18 g per person, which is very low compared to consumption of polymeric material (~7 kg) per person in the country. Thus, considering the growth of population and growth rate under different sectors of utilization of lac, a target of production of lac and shellac is to be fixed.

A consortium, of all concerned with lac, is needed to be formed, to develop strategies for achieving leadership in the global lac trade. Indian lac is inherently blessed to be the finest quality lac produced in the world compared to the lac produced by other countries. A world-wide awareness programme, is required to be undertaken regarding this unique property of Indian lac. Maintenance in quality of lac and lac-based products is to be ensured for building up confidence among foreign importers, similar to what Malaysia did for rubber industry. Some more suggestions include increase in production of lac, to make steady supply of quality lac; to increase domestic consumption; to reduce cost of production as well as processing; to reduce cost of all value added shellac; and selling of shellac and value added materials in sealed packet, introduction of quality declaration label on the packet, date of manufacture and date of expiry.

Strategies to reduce cost of lac and lac-based products

Prices of other natural resins and gums do not experience violent fluctuations, although these are totally export oriented commodity, most are exported in raw, unrefined form. The unsteady price of shellac is causing discouragement among users for its use in product development/ manufacture. Under the circumstance, reduction of cost of lac and lac-based products is desired to attract its consumers and to regain some of its lost ground. Some suggestions are: increase in production of lac; mechanisation of cultivation and post-harvest operations; installation of globally competitive plants in place of low capacity plants; reduction in the large labour force; building of infrastructure for storage (especially, AC) for common farmers for extending post-harvest life; and threat of cheaper imported lac for processing centres is to be overcome.

This Institute is ready to serve the nation and collaborate with all involved in the lac industries for the cause of sustained lac trade. Information from exporters and the industrialists regarding the researchable issues in the processing of lac or manufacture of any value added products, sector-wise consumption/demand of shellac in the domestic market and areas of consumption of shellac in foreign countries will be helpful in reorientation of research programmes of the Institute.

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